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CHARACTERISATION AND SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE SEDIMENTS OF BRISBANE RIVER

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STATEMENT OF ORIGINAL AUTHORSHIP

The work contained in this thesis has not been previously submitted for degree or diploma at any other tertiary educational institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signed: .....

(Kenneth. N. Ogogo)

Date: 24 October 2013

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ABSTRACT

Environmental pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), are known to result from increased urbanisation and act as indicators of anthropogenic activity in sediments from aquatic ecosystems. They are a main focus of environmental studies, especially in urbanised areas due to their persistence, bioaccumulative, and toxicity capabilities. Thus the characterisation of polycyclic aromatic hydrocarbons in sediment samples collected from Brisbane River was carried out in this thesis.

The PAHs compositional profile obtained was consistent with the diagnostic ratios analysis performed and showed the predominance of the (4-6 rings) higher molecular weight PAHs corresponding to compounds typical of high temperature combustion processes. In addition, a comprehensive data analysis was conducted using hierarchical cluster analysis and principal component analysis to identify similarities and patterns between the investigated PAH compounds. A multi-criteria decision-making method (MCDM), Preference Ranking Organisation Method for Enrichment Evaluation (PROMETHEE), coupled with a Geometrical Analysis for Interactive Assistance (GAIA) was applied in order to rank sampling sites and examine patterns in the data.

Results from the study were also subjected to source apportionment techniques using receptor model procedures which include: Principal Component Analysis-Absolute Principal Component Score (PCA-APCS) and Positive Matrix Factorization (PMF), to identify sources and contributions of PAH in surface sediments. The sources with

the largest contributions to the PAHs profile were diesel and traffic-related emissions, petroleum spillage (unburned petroleum) and urban runoff source. Multivariate statistical analysis clearly demonstrated that petroleum-related products made the greatest contribution to PAHs load in sediments.

The work presented in this thesis is based on the premise that (i) no comprehensive study has specifically been attempted to assess PAHs sources in the Brisbane River qualitatively and quantitavely since the 2011 flood, and (ii) information from source identification and apportionment study is required for source control and formulation of pollution mitigation measures To the best of our knowledge, this is the first application using the MCDM and source apportionment techniques for ranking and source identification of sampling sites and PAHs in surface sediments from urban rivers in Australia.

KEYWORDS: Sediment; Polycyclic Aromatic Hydrocarbons; Multivariate statistical analysis; Source apportionment; Brisbane River.

ABBREVIATIONS

Frequently used terms in this thesis include:

ACE: Acenaphthene

ACY: Acenaphthylene

ANT: Anthracene

ASE: Accelerated Solvent Extraction

B[b+k]F: Benzo(b+k)fluoranthene

BaA: Benzo(a)anthracene

BaP: Benzo(a)pyrene

BgP: Benzo(ghi)perylene

CHR : Chrysene

DBA: Dibenzo(a,h)anthracene

FLT: Fluoranthene

FLU: Fluorene

GAIA: Geometrical Analysis for Interactive Aid

GC: Gas Chromatography

HCA: Hierarchical Cluster Analysis

HPAH: High Molecular Weight Polycyclic Aromatic Hydrocarbon

IND: Indeno(1,2,3-c,d)pyrene

LOD : Limit of Detection

LPAH: Low Molecular Weight Polycyclic Aromatic Hydrocarbon

MCDM: Multi Criteria Decision Making

MDL: Method Detection Limit

NAP: Naphthalene

PAH: Polycyclic Aromatic Hydrocarbon

PCA: Principal Component Analysis

PCA/APCS: Principal Component Analysis/Absolute Principal Component Scores

PHE: Phenanthrene

PMF: Positive Matrix Factorization

POP: Persistent Organic Pollutant

PROMETHEE:Preference Ranking Organization Method for Enrichment Evaluation

PYR: Pyrene

SRM: Standard Reference Material

TEF: Toxic Equivalency Factor

TEQ: Toxic Equivalent Quotient

TOC: Total Organic Carbon

USEPA: U.S. Environmental Protection Agency

CHAPTER 1: INTRODUCTION

1.1. STUDY OVERVIEW

Organic chemical substances that are produced as by-products of anthropogenic activity are regarded as environmental pollutants. These contaminants may be present at low concentrations and have significant ecological impacts due to their ability to enter the aquatic food chain and bioaccumulate in the tissues of marine organisms (Froehner et al. 2011). These persistent organic pollutants (POPs) may include: pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs).

POPs have complex interactions with different environmental compartments as they can be dispersed in the atmosphere, dissolved in water, adsorbed onto sediments and accumulate in biota. They are also capable of long-range transport (LRT), resulting in their ubiquitous presence in the environment often at distances far from their origin (Klečka et al. 1998; Scheringer. 2009). The occurrence of these group of contaminants in the aquatic ecosystem have been observed from point (i.e, specific and identifiable sources of pollution such as direct oil spills, effluents from industrial facilities) and non-point sources (diffuse sources over a broad geographical scale such as atmospheric fallout and stormwater runoff) (Manoli et al. 1999; Pies et al. 2008). Assessment of organic contaminants in the aquatic environment is generally carried out to determine the potential risk posed to aquatic wildlife and potentially to humans (Daly et al. 2004). This will also enable a better understanding of the sources, distribution and fate of POPs in the urban environment.

POPs have specific physico-chemical properties that have resulted in distinct distribution patterns in the environment. In aquatic ecosystems, much of the focus has been on the environmental level and behaviour of PAHs due to their potential toxicity, carcinogenicity and mutagenicity (Nikolaou et al. 2009; Zhang et al. 2011). PAHs are of particular concern as a result of their persistence and their ability to volatilise and undergo long-range dispersion (Lehnik-Habrink et al. 2010; Shi et al. 2012). Previous environmental studies have shown the distribution of PAH in the aquatic environment where they are partially dissolved in water and in sediment at relatively high levels (Jaward et al. 2012). As a result, investigations of PAH have focused on sediments in urban water-sheds as they act as environmental sinks for adsorbed PAH compounds. In addition, they also serve as effective tracers of environmental contaminants and therefore, the distribution of PAHs in sediments provides a good measure of the quality of the aquatic ecosystem especially large urban water-sheds. As a consequence, the Brisbane River, Australia has been suggested as an ideal system for environmental monitoring of PAHs. A more detailed description of the PAH sources and characteristics has been outlined in the second chapter of this thesis.

1.2. DESCRIPTION OF THE STUDY AREA

The Brisbane River Catchment is the largest urbanised river system on the South-East coast of Queensland spanning an estimated distance of 344 km which covers a catchment area of about 13,600km^2. The catchment is fed by the Brisbane, Bremer, Lockyer and the Stanley Rivers and its source located in the foothills of the Great Dividing Range. The hydrodynamics are mainly controlled by a freshwater regime

upstream of the Wivenhoe Dam, and a saline tidal regime from Colleges crossing to its estuary at Moreton Bay. It is classified as a tide-dominated river (tidal range average of about 1·2 m) as it is influenced by tidal currents (Eyre et al. 1998), particularly along its main stem. Additionally, several major tidal tributaries connect to the main channel of the river before it empties into its estuary at Moreton Bay. These include like the Oxley, Breakfast, Bulimba's Creeks at the lower reaches and the Bremer Rivers located at the upper reaches of the river. The Brisbane River catchment is influenced by the sub-tropical climate that has two distinct wet summer and dry winter seasons with annual averages for temperature ranging from 15-25˚C and an annual average rainfall of about 940 mm (Eyre et al. 1998). The River is also characterised by high turbidity mostly due to the tidal pumping of resuspended sediments which has previously been estimated to have an annual sedimentation rate of around 140000 tons/year (Marston. 2000).

The Brisbane River catchment has been broadly classified into upper, middle and lower sections and these are associated with distinct land uses. The upper catchment is removed from anthropogenic influences and considered to be predominantly rural and pristine. Similarly, the middle-catchment has been historically considered a rural transect of the river as it is mostly surrounded by land mainly used for intensive agriculture and grazing but has been moderately urbanised in recent years. The lower catchment is noted as the heavily urbanised and industrialised section of the river as it passes through the city and the major industrial areas.

1.3. CURRENT STATUS OF THE BRISBANE RIVER

The overall study area has been described previously by Kayal et al (1990) and Shaw et al (2004). It covers a distance of about 40 kilometres and extends from the upstream reaches of Oxley to its estuarine point at the Fisherman's Island (Port of Brisbane). The study area was also situated around the metropolitan Brisbane city, one of the fastest growing economic capitals in Australia and, supports the largest population of any river catchment in the state of Queensland.

The study area (Figure 1-1) represents the most urbanized and industrialised transect of the Brisbane River and is strongly impacted by anthropogenic activities around its shorelines. Such activities include chemical and petrochemical works, sewage treatment facilities, boat building and repair yards, paper recycling plant, heavy vehicular and maritime traffic and infrastructures such as wharves and fuel piers, dredging and recreational parklands. These anthropogenic activities may lead to major environmental concerns as they mostly result from the discharge of industrial wastewater, accidental oil spills, municipal and urban runoff, and atmospheric precipitation, causing contamination with ubiquitous environmental contaminants such as PAHs (Xu et al. 2007). Their persistence in the aquatic ecosystem is largely recorded in sediments which act as the final sink, enabling the impact of the anthropogenic activities to be readily monitored. As a result, the sources, occurrence, transport, and fate of PAHs in aquatic environment has been extensively investigated around the world (Vane et al. 2007; Viñas et al. 2010; Prabhukumar. 2011; Wang et al. 2011; Wang et al. 2012).

Figure 1-1: Map showing the location of sampling sites and major creeks in the Brisbane River. Source: (Adapted from Bing maps) Harris Corp, Earthstar Geographics LLC © 2013 Microsoft Corporation)

Similar PAH studies have been conducted in Australia, especially in the urban rivers of Queensland, Victoria and New South Wales (Kayal. 1990; Brown et al. 1992; McCready et al. 2000; Shaw et al. 2004), where available data regarding the sedimentary record of PAHs have been obtained. These investigations were centred on the sixteen (16) PAH parent compounds described by the United States Environmental Protection Agency (USEPA) as "priority pollutants" (Nikolaou et al. 2009). They include: low molecular weight PAH (LPAH) compounds namely; naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT) and high molecular weight PAH (HPAH) compounds fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IND), dibenzo(a,h)anthracene (DBA) and benzo(ghi)perylene (BgP) (Figure 2-1).

Previous investigation on the occurrence of organic contaminants in the Brisbane River has led to an extensive focus on PAH distribution in the water, sediments and biota compartments (Kayal. 1990; Muller et al. 1999; Shaw et al. 2004). Shaw et al (2004) recently focused on monitoring of PAH in aquatic sediments, with a particular aim of evaluating their concentration levels within a specific time period (spring and summer seasons). Thus, PAH levels in the Brisbane River have been characterized by identifying their concentration and spatial distribution across various investigated sites. However, there is paucity of information regarding recent PAHs distribution in sediments in the river especially after the January 2011 floods. Furthermore, none of the previous studies employed source apportionment techniques for the identification and quantitative evaluation of PAH sources in the

river. Therefore, in view of the pollution condition and significance of the investigated watershed, the characterization of PAHs and their sources by receptor models was considered a novel approach that could significantly contribute to the understanding of the primary source(s) of PAHs in sediments.

1.4. STUDY OBJECTIVES AND THESIS OUTLINE

The overall aim of the study was to identify and apportion the major sources of PAHs in the Brisbane River allowing for comparison with the previous reports on sedimentary PAH contamination. The specific study goals were;

- To identify and estimate the distribution and contamination level of PAHs

- To identify and characterise the possible sources of PAHs in sediments by means of source apportionment techniques

This thesis consists of five chapters as follows: Chapter 1 provides a rationale for current study that includes: information and shortcomings of previous PAH investigations associated with the study area and the current study objectives. Chapter 2 provides an exhaustive literature review on the nature of the present study and trends in PAH investigation. It describes the occurrence and sources of PAHs in the environment, exploring their relevant physicochemical properties and the potential toxicity risk to their exposure.

Chapter 3 describes the overall sampling methodology and analytical procedures applied. Chapter 4 describes the data analysis and provides interpretation and discussion of the pollutant distribution data employing a combination of univariate statistical analysis, chemical fingerprinting and chemometric techniques. These include: Diagnostic ratio indices, Principal Component Analysis (PCA), and Clustering Analysis (HCA) used in pattern recognition. In addition, receptor modelling techniques such as Principal Component Analysis - Absolute Principal Component Scores (PCA-APCS) and the Positive Factorisation Matrix were applied for PAH source apportionment, while a multi-criteria decision making approach was employed to facilitate site ranking in view of the study area and pattern recognition among the investigated PAHs. Lastly, Chapter 5 provides the concluding comments and suggestions for future studies.

CHAPTER 2: REVIEW OF LITERATURE

2.0. INTRODUCTION

This chapter reviews the literature relevant to polycyclic aromatic hydrocarbon (PAHs) in the environment and in particular, the aquatic ecosystem. It describes the environmental occurrence, sources and common uses of PAHs. It also points out some important physical and chemical characteristics and provides some insights into their environmental adverse effects and toxicity criteria. Finally, it provides trends and the gaps in the literature addressed by current study.

2.1. ENVIRONMENTAL OCCURRENCE

The determination of the levels and sources of PAHs in the urban environment has been a major focus of environmental monitoring and assessment studies (Ravindra et al. 2008; Mostert. 2008; Huang et al. 2012), which have examined their prevalence in various environmental compartments, especially in circumstances where they occur at low concentrations but are biologically potent (Bostrom et al. 2002).

PAHs represent a large group of relatively non-polar, hydrophobic organic compounds that are composed of two or more fused aromatic rings containing carbon and hydrogen atoms (Nikolaou et al. 2009; Liu et al. 2012). PAH are ubiquitous and can be found in the vapour and particulate phase in the atmosphere, and are readily found in the solid and dissolved phase in soil, sediments and surface water. They are regarded as the most stable form of hydrocarbons having low

hydrogen-to-carbon ratio found in complex mixtures rather than single compounds (Ravindra et al. 2008).

PAHs can be divided into two classes: low molecular weight (LPAH) and high molecular weight PAHs (HPAH). LPAH consist of compounds such as naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene and tend to be made up of two or three benzenoid ring core structure. In contrast, HPAH are made up of molecular structures of four or more benzenoid rings, such as: fluoranthene, pyrene, benzo[a]pyrene, and benzofluoranthenes. They are further classified depending on their substitution with one or several different functional groups such as amino-, chloro-, cyano-, hydroxyl-, oxy- or thio groups (Bergvall. 2009). Hundreds of possible PAH isomers have been reported in the environment (Ramesh et al. 2004).

2.2. MECHANISM FOR PAH FORMATION

PAH may be synthesized from saturated hydrocarbons under oxygen-deficient conditions (Ravindra et al. 2008), as shown in simple PAH mechanism, resulting from a stepwise formation of an alkane (Figure 2-2). The number of alkyl carbon atoms present in the side chain and relative abundances of individual PAH varies with the temperature at which they are formed (Mastral et al. 2000).

Two primary mechanisms (pyrolysis and pyrosynthesis) are responsible for the formation of PAH in the environment. Pyrolysis involves the combustion of organic materials such as crude oil at high temperatures resulting in small unstable fragments

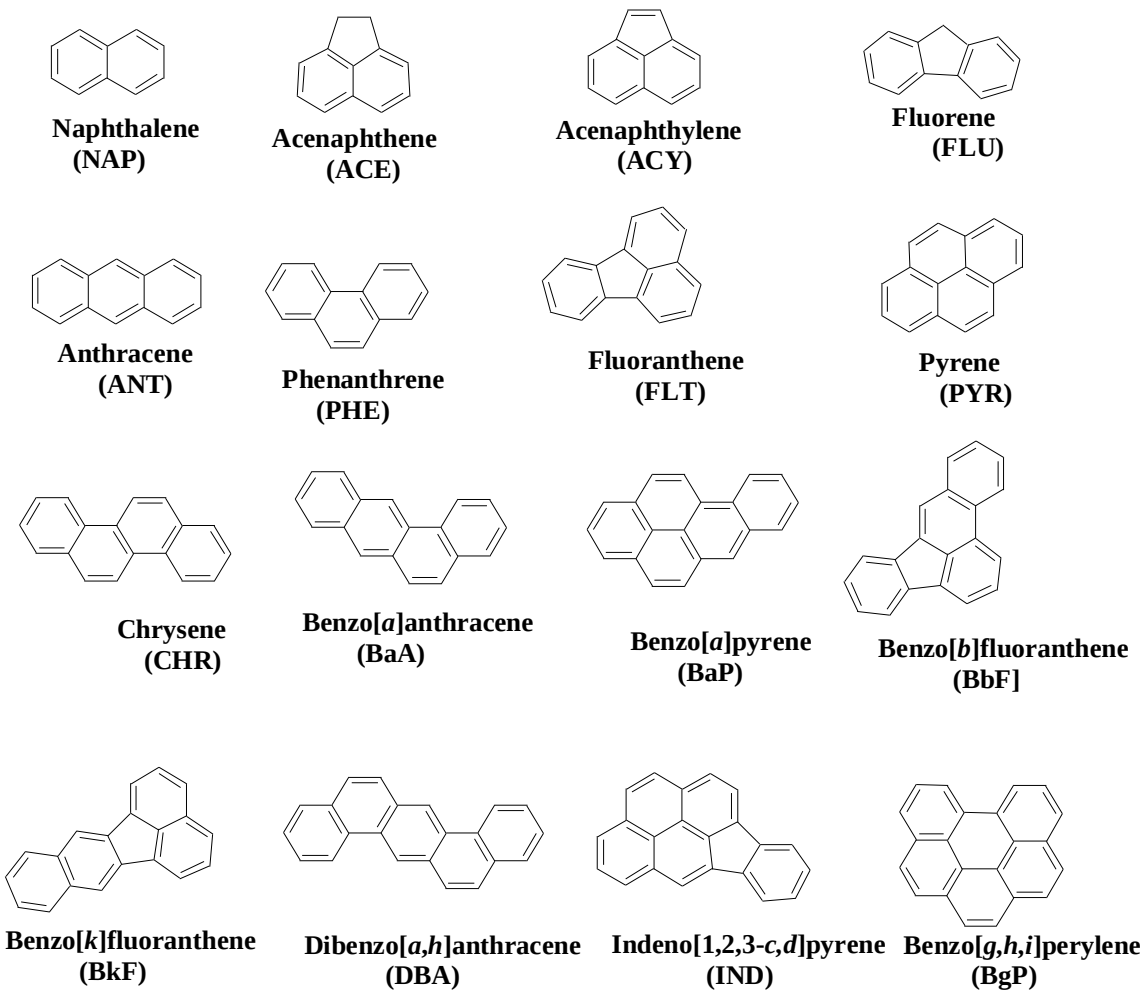


Figure 2-1: Structures of the priority PAH compounds

(Abrajano et al. 2004). On the other hand, pyrosynthesis also involves the formation of PAH at higher temperatures (> 500^0C) from carbon–hydrogen and carbon–carbon bond that are broken to form free radicals. The free radicals are unstable fragments that undergo bimolecular reactions with unsaturated hydrocarbons such as alkenes and alkynes to form large ring structures resistant to thermal degradation (Britt et al. 2004; Ravindra et al. 2008).

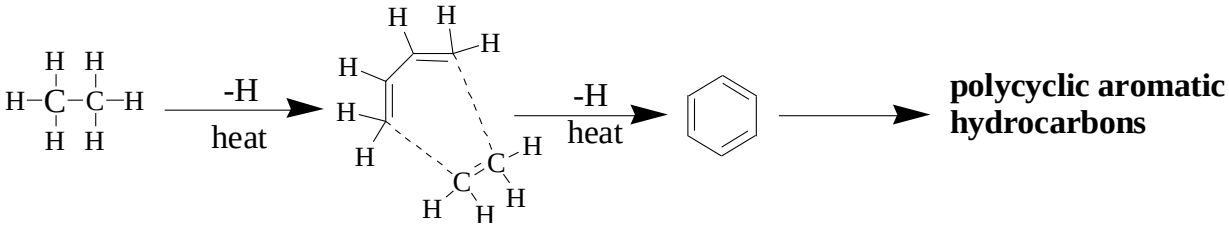


Figure 2-2: Pyrosynthesis of PAHs starting with ethane. Adapted from (Ravindra et al. 2008)

2.3. SOURCES OF PAHs

PAH sources can be classified as natural or anthropogenic sources. The natural sources include diagenic sources (formed from plant precursors) and biogenic sources (formed from microbial degradation), whereas the anthropogenic sources include petrogenic sources (PAH formed at low temperature over geological time scale or direct spillage of petroleum product) and pyrogenic sources (PAH, formed during the incomplete combustion processes). PAH sources are also associated with their use as intermediaries in industrial processes in the production of consumer products as listed in Table 2-1.

2.3.1. Naturally Occurring PAHs

PAH formation from natural processes occur from direct biosynthesis in plants and aquatic microorganisms and as a result of low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel (Prabhukumar. 2011). However, PAH formed through biosynthesis have relatively lower concentrations compared to those formed by combustion processes (Richter et al. 2000; Lima et al. 2005). They include compounds such as perylene and retene, which are noted as diagenic and biogenic PAH (Abrajano et al. 2004; Anyakora et al. 2011). However, both compounds have been linked to potential PAHs combustion sources (Wang et al. 1999; Liu et al. 2005; Petrisic et al. 2013).

Perylene an unsubstituted 5-ringed pentacyclic PAH is found pervasively in both marine and freshwater sediments and is formed as a result of diagenesis (i.e, chemical, physical, or biological change) (Abrajano et al. 2004; Macías-Zamora et al. 2002; Silliman et al. 1998; Iqbal et al. 2008) . Perylene has been reported to be formed under prevailing reducing conditions from the conversion of terrestrial dihydroquinone pigments within sediments depositional areas (Kayal. 1990). In a recent study, Boonyatumanond et al. (2006) described the formation of perylene in anoxic sediment to result from a reduction of perylenequinone (Boonyatumanond et al. 2006). In contrast, retene is associated with terrestrial organic matter formed as an end product from wood combustions (Abrajano et al. 2004) and also from the dehydrogenation of abietic acid, a major constituent of coniferous resins (Zhou et al. 2000).

Naturally occurring PAH such as perylene has been compared with anthropogenic PAH. However, PAH investigations have excluded anthropogenic activities as possible sources due to the fact that the historical trend of perylene recorded in sediment cores differed from those of anthropogenic PAHs (Silliman et al. 1998; Liu et al. 2012). However, perylene has recently been reported in South Louisiana crude oil sources (Iqbal et al. 2008) and in lower concentrations in car soot samples (Abrajano et al. 2004). Other biogenic precursors include an extended series of phenanthrene homologues, tetra- and penta-cyclic PAHs that are observed in sediments (Morgunova et al. 2012). In general, the diagenic PAHs are frequently found at background levels in recent sediments and often dominate the assemblage of PAHs as a result of historic sediments deposition.

2.3.2. Anthropogenic PAHs

The two predominant anthropogenic sources of PAHs are classified as petrogenic and pyrogenic. PAHs from pyrogenic sources are generally produced from the incomplete combustion of fossil fuels whereas, the petrogenic sourced PAHs (from petroleum origin) consist mainly of crude and refined petroleum products (Abrajano et al. 2004).

2.3.2.1. **Petrogenic PAH Sources**

These mainly consist of lower molecular weight congeners (LPAH), characterised by the predominance of two or three fused benzene rings and an abundance of substituted PAHs, in particular homologues with two to three alkyl carbons (Neff et

al.2005). The alkylated (i.e., possessing alkyl side chains) homologues are typically represented in higher proportions relative to the parent PAH such that the ratio of the sum of methyl-phenanthrene isomers relative to phenanthrene (MPhe/Phe) is always greater than one (Stout et al. 2001; Liu et al. 2005; Saha et al. 2009; Oyo-Ita et al. 2011).

The two major sources of petrogenic PAHs in the aquatic environment are found from the indiscriminate dumping of waste crankcase oil and the leakage of crankcase oil drippings onto road surfaces with subsequent washout by road runoff (Zakaria et al. 2002). The molecular distribution of PAHs in petroleum and crankcase oil serves as a good basis for source identification of the lower polycyclic aromatic hydrocarbons (LPAH), while other potential sources of petrogenic PAHs identified in the environment are believed to be present in petroleum-based products such as asphalt, tyre and brake lining particles (ATSDR 1995). Furthermore it is worthy to note that the petrogenic PAHs are characterised as being non-persistent in nature and therefore, less likely to be found in environmental components such as particulate matter and sediments (Abrajano et al. 2004).

2.3.2.2. **Pyrogenic Sources**

PAHs derived from pyrogenic sources are made up of higher molecular weight compounds (HPAH) and consist of up to four to six fused benzene rings. They are naturally produced in the environment by forest and grassland fires, but their largest source is through anthropogenic activities (Liu et al. 2012) at relatively higher temperatures (400−600°C). In a recent review, Lima et al (2005) suggested that

activities such as the combustion of organic material were the dominant source of PAH in recent sediments. These activities are associated with industrial processes such as coke production, manufactured gas production, aluminium smelting, and creosote production.

In general, the pyrogenic sources of PAHs make up a higher mass percentage and are quiet distinct from petrogenic PAHs sources. Additionally, their relative stability to environmental factors such as weathering, biodegradation and persistence in the environment enables easier discrimination from petrogenic PAH sources (Yunker et al. 2002).

2.4. PHYSICOCHEMICAL PROPERTIES OF PAHs

Fundamental properties of PAH related to their physicochemical behaviour have been well characterised (Nikolaou et al. 2009). Individual PAHs differ significantly in their physicochemical properties, such molecular weights, melting and boiling point, vapour pressure, water solubility and octanol-water coefficient as shown on Table 2-1. These physiochemical properties determine the fate of PAHs in the environment and their incorporation as ubiquitous environmental contaminants (de Maagd et al. 1998; Guo et al. 2011b; Guo et al. 2011a). Despite the numerous PAH investigations conducted in the literature, an exact mapping of their distribution in the various environmental compartments remains complex. There is a continuous distribution of PAHs in the different compartments of the environment where they undergo a myriad of transformations as a result of their physicochemical properties. The important properties that govern the transport and distribution of PAHs in the

environment include: water solubility, volatility and octanol-water partition coefficient (K_{ow}) and degradation.

(a). Water Solubility: PAHs are generally hydrophobic in the aquatic environment with solubility in aquatic matrices decreasing with increasing molecular weight (Nikolaou et al. 2009). Therefore, the higher molecular weight PAHs tend to be relatively insoluble in water.

(b) Volatility: (Henry's Law Constant): This is a measure of the ability of a compound to partition between air and water phases. A direct relationship exists between the Henry's law constant and vapour pressure with a high "H" constant value accounting for high volatility. An increase in the ring number of the PAHs corresponds to a decrease in their vapour pressures. As a consequence, the HPAH do not undergo insignificant volatilisation (Lundstedt. 2003).

(c) Octanol-Water Partition Coefficient (K_{ow}):

This is the ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase. An inverse relationship exists between aqueous solubility and $K_{ow.}$ PAHs with low K_{ow} values are readily soluble in water, while PAHs with higher values of (K_{ow}) are hydrophobic and associate with particulate matter, hence show a greater tendency to adsorb into sediments (Litskas et al. 2012). For example, naphthalene (2-ring PAHs) has a log K_{ow} value of 3.37, while benzo(ghi)perylene (6-ring PAHs) possesses a higher log K_{ow} value of 6.50 (Table 2.1). Therefore, naphthalene is more water soluble than benzo(ghi)perylene.

In summary, octanol-water partition coefficient (K_{ow}), partition, Henry's Law constant and aqueous solubility are specific properties that are directly relevant in predicting the environmental fate of a PAHs (Prabhukumar. 2011; CCME 2008).

2.5. FATE OF PAHs INTO THE AQUATIC ENVIRONMENT

The aquatic environment serves as a major compartment for potentially toxic anthropogenic compounds (Woodhead et al. 1999). The introduction of PAHs into the aquatic environment has been a cause of concern due to potential adverse health and environmental effects. This is further exacerbated as a number of important transport and transformation processes occur at the air-water and water-sediment interfaces of the environment (Chen. 2008). Contaminant distribution processes such as surface discharge and atmospheric deposition have been indicated as environmental factors which aid PAH mobility (via deposition/resuspension processes) in the aquatic ecosystem (Van Metre et al. 2000; Liu et al. 2009b; Dupree et al. 2007).

2.5.1. Deposition of Atmospheric PAH

Atmospheric deposition is a recognized pathway of PAH inputs into the environment and can result in their distribution over long distances without significant degradation (Simcik et al. 1999). The important role played by the air-water interface which acts in the transfer of substances between the atmosphere and surface water and its effect on the distribution and eventual fate of PAHs has been previously demonstrated in the aquatic environment (Liu et al. 2005; Silliman et al. 1998).

Table 2-1: Physical and chemical characteristics of the priority EPA PAHs Adapted from (ATSDR. 1995)

Compounds	Molecular Weight ($gmol^{-1}$)	Vapor pressure (mm Hg)	Water Solubility (mg/1)	Henry's Law Constant ($atm\text{-}m^3/mol$)	Melting Point (^oC)	Boiling Point (^oC)	Log K_{ow}
Naphthalene	128.17	-	0.021	$4.83x10^{-2}$	80.2	218	3.37
Acenaphthylene	152.2	3.87	3.93	$1.45x10^{-3}$	92-93	265-275	4.07
Acenaphthene	154.21	$5.96x10^{-1}$	1.93	$7.91x10^{-5}$	96.2	279	3.98
Fluorene	166.22	$4.27x10^{-2}$	1.68-1.98	$1.0x10^{-4}$	116	293-295	4.18
Phenanthrene	178.23	$9.07x10^{-2}$	1.2	$2.56x10^{-5}$	100	340	4.45
Anthracene	178.23	$2.27x10^{-3}$	0.076	$1.77x10^{-5}$	218	340	4.45
Fluoranthene	202.26	$6.67x10^{-4}$	0.20-0.26	$6.5x10^{-6}$	110	384	4.9
Pyrene	202.26	$3.33x10^{-4}$	0.077	$1.14x10^{-5}$	156	393	4.88
Benzo(a)anthracene	228.29	$2.93x10^{-6}$	0.01	$1x10^{-6}$	162-167	435	5.61
Chrysene	228.29	$8.40x10^{-5}$	$2.8x10^{-3}$	$1.05x10^{-6}$	255-256	448	5.16
Benzo(a)pyrene	252.32	$7.47x10^{-7}$	$2.3x10^{-3}$	$4.9x10^{-7}$	179	495	6.06
Benzo(b)fluoranthene	252.32	$6.67x10^{-5}$	0.0012	$1.22x10^{-5}$	167	357	6.04
Benzo(k)fluoranthene	252.32	$8.79x10^{-9}$	$7.6x10^{-4}$	$3.87x10^{-5}$	215-217	480	6.06
Indeno(1,2,3-cd)pyrene	276.34	$1.33x10^{-9}$	0.062	$6.95x10^{-8}$	161.5-163	530	6.58
Dibenzo(a,h)anthracene	278.35	$1.33x10^{-9}$	$5x10^{-4}$	$7.3x10^{-8}$	266-267	524	6.84
Benzo(g,h,i)perylene	276.34	$1.37x10^{-8}$	$2.6x10^{-4}$	$1.44x10^{-7}$	278	500	6.5

Three major atmospheric processes for PAH entry into the aquatic system have been identified as (a) wet deposition via rain, snow and fog (b) dry deposition of particles and (c) gaseous phase, as well as dissolved or suspended in precipitation (Golomb et al. 2001; ESA. 2004). However, dry deposition predominates; in more remote areas, wet deposition predominates, mostly in urban/industrial areas (Golomb et al. 1997). Upon entry onto the atmosphere, PAH are redistributed between gas and particle phases with LPAH tending to concentrate in the vapour-phase while HPAH are more likely to associate with particulates (Wang et al. 2010). The presence of PAH in the atmosphere are generally governed by their sizes and the long-range transport of particulates that eventually gets removed by the process known as "atmospheric fallout" (Fang et al. 2006). In general, industrial activities are shown to be the major contributors of PAHs into the atmosphere (Table 2-2).

Table 2-2: Industrial point sources of PAHs (WHO. 1998)

Industrial Sources	PAH Type
Power Plants using fossil fuel	NAP,ACY,ACE, ANT,FLT, PYR, BaA, CHR, BbF, BkF BaP, IND, and BGP
Incinerators	BaA, CHR, FLU
Aluminium Production	NAP, BaP, BgP
Iron & Steel Production	NAP,ACY,ACE, ANT,FLT, PYR, BaA, CHR, BbF, BkF BaP, IND, and BGP
Foundries	ANT,FLT, PYR,CHR, BbF, BaP, IND, BGP

Higher concentrations of PAHs have been observed to result in increased precipitation, showing apparent resistance to degradation. As a result, low to-moderate concentration levels of PAHs have been found in pristine watersheds far

away from anthropogenic sources (Wang et al. 2010). Emissions from mobile anthropogenic sources such as gasoline and diesel engine exhausts) and stationary anthropogenic sources (e.g. coal-fired power plant, residential heating) sources (Ravindra et al. 2008; Lee et al. 2010), have been noted to be major contributors of PAH to the environment. Recently, Guan et al (2012) suggested atmospheric deposition to be a major source of PAH input ranging from 473.9-2289 ng/g in lake sediments. Similarities in PAH composition between sediments and particulates in the atmosphere were strongly linked.

The residency time of the PAH in the atmosphere and transport to different geographic locations depends on factors such as the PAH concentration, atmospheric temperature, the organic carbon partition coefficient (K_{oc}). As a result, the LPAH (2-3ring) constitute the dominant species in the gaseous phase of PAH in the atmosphere and appear to be less strongly adsorbed to atmospheric particles. In contrast, the HPAH readily exist in the particulate phase, and as a result of dry deposition and particle fallout, they are subsequently transferred into water surfaces, ultimately accumulating in sediments (ATSDR. 1995; Kim et al. 2009). In a previous investigation at the Georges River Estuary in Sydney, PAHs in sediments were found to originate from combustion sources associated with atmospheric particles (Brown et al. 1992). Furthermore, in recent studies conducted on continental shelf sediments from the Yellow Sea in China, it was observed that the occurrence of anthropogenic PAH in the water column could be attributed to the high PAH concentrations in the deposits of atmospheric flux. Higher levels of anthropogenic PAHs during atmospheric transport and subsequent deposition into the aquatic environment were further suggested to be a result of regional input and

environmental factors, such as sediment organic carbon content and sedimentation rate (Liu et al. 2012). Atmospheric deposition was also shown to be the cause of high concentrations of PAH in a study based on sediments from the Massachusetts Bay, USA (Golomb et al. 2001).

2.5.2. Surface Discharge of PAHs

PAHs reach surface water via non-point sources such as urban runoff and point sources such as oil spillages, industrial effluents and wastewater treatment plants that are located near watersheds (Yunker et al. 2002; Neff et al. 2005). PAHs that are mainly transported by surface discharge occur in both particulate and soluble phase, but mostly found in the particulate phase due to their low solubility and hydrophobic nature (Kim et al. 2009).

Runoff has been reported to be a major delivery system of anthropogenic PAH into the aquatic ecosystem (Grapentine et al. 2004; Rojo-Nieto et al. 2013). Factors such as rainfall and sewer disposal carry particulates containing moderate levels of PAHs in urban runoff, reportedly playing a key role in the degradation of aquatic systems in urban areas (Herngren et al. 2010). In other words, surface discharge has been observed as a consistent and ongoing source of PAHs to marine sediments (Nikolaou et al. 2009), thereby facilitating their accumulation in the aquatic ecosystem. Additionally, PAHs in surface discharges resulting from increased volume and intensity of surface runoff (i.e. urban runoff) have also been known to occur in both the particulate and dissolved forms, although studies have shown particulate forms as the most predominant (Prabhukumar. 2011; Bathi et al. 2012).

Van Metre et al. (2000) reported the increasing PAH levels in freshwater sediments; as with discharges associated with industrialization and urbanization as important entry routes into the aquatic environment. McCready et al. (2000) investigated PAH contamination from stormwater runoff and its resultant effect in the contamination of surface sediment in the Sydney Harbour. The observed PAH concentrations varied widely (< 100 to 380,000 μg kg^{-1}) indicating an increase in PAH concentrations at points where urban stormwater flows into the river. In a previous study conducted on an assessment on airport runoff, high PAH concentrations were observed to range between 180–6,758 ng/l (Sulej et al. 2011). Consequently, urban runoff is an important source of PAH contamination in sediments from the aquatic environment.

2.6. TRANSFORMATION PROCESSES

2.6.1. Photooxidation

Photooxidation refers to light-assisted chemical reactions that can affect compounds in the atmosphere and in the photic zone of surface water and are regarded as one of the most important process leading to PAH degradation in water (Abrajano et al. 2004). While, PAH compounds are relatively stable due to their delocalized π-electron cloud and large resonance energies, it has been suggested that they undergo photochemical reactions by strongly absorbing visible (400–700 nm) (Mallakin et al. 2000) and UV light (313 and 366nm) (Fasnacht et al. 2002). PAH compounds can absorb surface solar radiation directly, enabling photo-transformation of PAH by a-singlet oxygen to form various oxygenated intermediates products such as diones which are often more biodegradable than the parent compounds (Nkansah. 2012).

The photolysis rate of PAHs in aquatic matrices has been shown to be relatively fast compared to their corresponding rate in the atmosphere (Kot-Wasik et al. 2004). In a previous study, the influence of advanced oxidation processes (AOPs) which includes direct photolysis and radical oxidation was observed for the degradation of LPAH such as acenaphthene, phenanthrene and fluorene (Beltran et al. 1995).Similarly, the decomposition of HPAH such as chrysene and benzo(a)pyrene, present in aqueous media by means of photolysis was investigated The rate of degradation was determined by competition between PAH intermediate and their initial substrates for light (Miller et al. 2001). McConkey et al. (2002) described a mechanism for electron transfer oxidation through excitation of anthracene-oxygen contact charge transfer pairs, in which the photoproducts were composed of mainly anthraquinones and phenols.

2.6.2. Biodegradation

This refers to the microbial degradation of PAHs in the environment (Rojo-Nieto et al. 2012) and also serves as a major PAH degradation process (Xia et al. 2006;Haritash et al. 2009; Prabhukumar. 2011), particularly in soil and sediments. It involves the transformation of PAH mainly in polluted soil and/or sediment from the production of extracellular lignin-degrading enzymes to detoxified metabolites by a wide variety of microorganisms such as bacteria, fungi and algae (Abrajano et al. 2004; Haritash et al. 2009)

Biodegradation of PAHs depends on factors such as their physical and chemical properties, physicochemical parameters of the site as well as the characteristics of

microorganisms present. In other words, the biodegradation potential of PAHs generally increases as their molecular weight increases (Rojo-Nieto et al. 2012). However, biodegradation half-lives of PAH with more than three rings have been considered to be longer (143-812 days)than the PAHs with three or fewer rings (33-88 days) Macrae et al 1998, as the rate of sorption of the higher molecular weight PAHs by soil organic matter may limit their biodegradation when metabolised by microorganisms.

The degradation pathways of HPAH such as fluoranthene (FLT), pyrene (PYR), and benzo(a)anthacene (BaA), chrysene (CHR), are less well understood but are thought to occur more slowly due to their resistance to microbial degradation processes resulting in their greater persistence in environment (Boonchan et al. 2000; Abrajano et al. 2004; Xia et al. 2006).

2.7. TRANSPORT PROCESSES

2.7.1. Sorption

Sorption involves exchange between water and the particulate phases and it is an important transport process for PAH. Sorption on sediments involves absorption or adsorption processes resulting in surface attachment or subsurface dissolution, respectively. Sorption coefficients are used to predict the fate of PAH in the aquatic ecosystem and also shown to be dependent on other factors such as the PAH origin, molecular weight and polarity (Abrajano et al. 2004; Brion et al. 2005).

The extent of preference by an hydrophobic contaminant for the solid surface is described in terms of the sorption coefficient (K_d) and is indicative of the quantitative distribution between the aqueous and solid phases of the system at equilibrium (Bathi et al. 2012). In summary, PAH physiochemical properties have been linked to play a critical role in sorption. In a recent study, Yang et al. (2011) described the sorption mechanism of PAH in natural sediment, whereby a relatively low sorption capacity for LPAH when compared with the HPAH was subsequently observed (Yang et al. 2011).

2.7.2. Volatilization

This refers to the evaporation of semi volatile organic compounds from surface water and their subsequent transport into the atmosphere. As previously discussed, this process is largely controlled by physical properties such as the value of the ratio of the Henry's Law constant relative to the octanol–water partition coefficient (H/K_{ow}) for a particular PAH compound (Cousins et al. 1999). Volatilization, primarily involves the loss of volatile compounds in an environmental compartment. Hence, it serves as a means by which volatile PAH compounds are removed from the aquatic ecosystems (Wild et al. 1995).

2.8. DISTRIBUTION OF PAHs IN SEDIMENTS

Globally, PAH fingerprints in aquatic sediments (i.e. river, marine and lake sediments) are shown to be similar and typical of high temperature pyrolysis (McCready et al. 2000). In addition, the aromatic structure of PAHs determines their

stability under reducing conditions in the aquatic environment, while their composition in sediments is dominated by the HPAH in contrast to the LPAH. PAH concentration in sediments is also reported to vary across different locations, thereby reflecting the degree of urbanisation (Dupree et al. 2007). Generally, as a result of their persistence and hydrophobicity in aquatic matrices, PAH adsorption in sediments leads to partitioning in organic carbon particles and accumulation to high concentrations in biota, where they serve as good biomarkers for gauging recent and historical anthropogenic contributions to the aquatic environment (Mitra et al. 1999; Witt et al. 1999; Viguri et al. 2002). Hence, the assessment of PAH concentrations in aquatic sediment serves as an important approach for monitoring the health of the aquatic ecosystem (Xu et al. 2007).

2.9. HEALTH EFFECTS OF PAHs

2.9.1. Exposure of PAH in the Environment

Several comprehensive studies have reported on the exposure effects of PAHs and the potential threat they pose to the health of ecological receptors (microorganisms, terrestrial plants and animals, aquatic biota) and consequently humans in the food chain (Delistraty. 1997). However, humans are mostly exposed to PAH at low concentrations (Binková et al. 2004). PAH exposure in the environment has been reported to induce a number of acute (sudden onset) and chronic (longer onset) effects. Acute effects include eye irritation, nausea, vomiting, and diarrhoea. Chronic effects may include cataracts, renal and hepatic damage, carcinogenicity and genotoxicity (Pickering. 1999).

2.9.2. Metabolism of PAHs

PAH are relatively inert compounds that require activation by xenobiotic-metabolizing enzymes into reactive metabolites such as Cytochrome P450 (CYP), which covalently binds to cellular DNA to exert carcinogenic effects. The reactive metabolites are linked to the metabolic activation of PAHs to epoxide intermediates, which are eventually converted to harmful carcinogens (Figure 2-3). Furthermore, the carcinogenicity of PAH mixtures may also be influenced by synergistic and antagonistic effects with other compounds that are co-emitted together mostly during the incomplete combustion processes.

Emphasis on carcinogenic and environmental concerns about PAHs such as BaP, which is regarded as a potent animal and probable human carcinogen have increased (Irwin et al. 1997). For example, benzo(a)pyrene (BaP) is believed to form carcinogenic metabolites, which bind to DNA forming a structures such as BaP-DNA adducts that can interfere with or likely alter DNA structure (ATSDR. 1995). Carcinogenic PAHs such as benz[a]anthracene (BaA) benzo[b]fluoranthene (benzo[k]fluoranthene (B[b+k]F), benzo[a]pyrene (BAP), dibenz[a,h]anthracene (DBA), indeno[1,2,3-cd]pyrene (IND) are present in different environmental compartments, especially in sediments where they accumulate in marine organisms and can lead to exposure in higher tropic animals as aresult of bioaccumulation via the environmental food chain (Juhasz et al. 2000).

2.9.3. Toxicity effects in the Aquatic Environment

A wide coverage has been laid down in the scientific literature regarding the exposure of aquatic organisms and animals such as bottom-dwelling invertebrate and fish to PAHs (Delistraty. 1997). The toxic effect of PAHs in these organisms may be attributed to chronic exposure of organisms to relatively high level of PAH compounds or their metabolic products which bind irreversibly to lipophilic sites within cell membranes in microorganisms (Solé et al. 2000). Scientific reports have demonstrated the toxicity effect on aquatic organisms of PAHs in sediments, whereby high levels have led to altered benthic community species composition by way of reduced growth and decreased survival rate (Holdway. 2002).

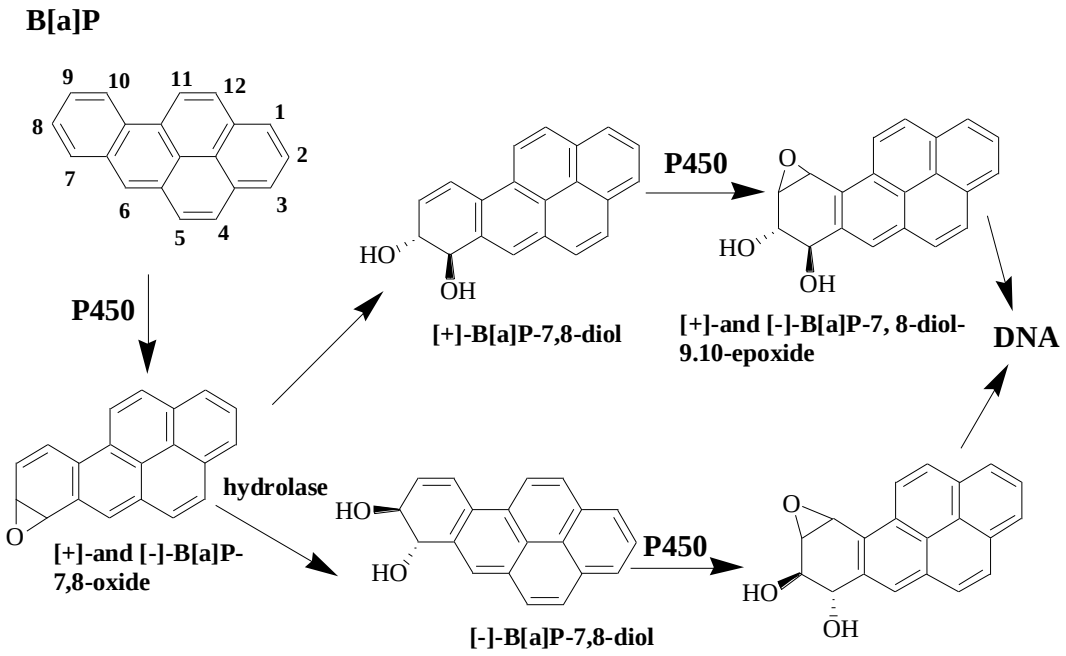


Figure 2-3: Pathway for the Metabolic activation of carcinogenic benzo(a)pyrene compound. Used with the permission of (Shimada et al. 2004) and Wiley Online Library

Similarly, high toxicity can cause physiological changes that may affect the swimming ability, growth and reproduction of aquatic animals such as fish. For example, high accumulation of PAH in fish tissues have been strongly associated with hepatic lesions and liver neoplasm (Johnson-Restrepo et al. 2008; Uno et al. 2010).

The harmful effect that PAHs have on the aquatic ecosystem depends on factors such as acute and chronic toxicity effects that are commonly based on the measurement of the median lethal concentration values (LC_{50}), which is a standard measure of the toxicity of a surrounding medium. In this regards, measured acute toxicity of PAHs based on the LC_{50} is observed to increase with increasing PAH molecular weight. The LC_{50} values are typically used to evaluate the nature of the toxicological interaction of PAHs based on extrapolation of sediment spiking exposures in a marine amphipod species such as *Rhepoxynius abronius* (Swartz et al. 1997). The acute and chronic estimates of the PAHs are listed in Table 2.4.

2.9.4. Toxicity Evaluation of PAH in Aquatic Sediments

2.9.4.1. **Sediment Quality Guidelines**

In the last decade, chemical and ecotoxicological data on environmental contaminants have been used to develop sediment quality guidelines (SQGs) in marine ecosystems (Viñas et al. 2010). These have been developed for a variety of pollutants and can be used depending on the purpose of the assessment, e.g., human health and/or aquatic life risk (Liu et al. 2009a).

Table 2-3: Estimated acute and chronic toxicity of PAHs and their carcinogenic potency classification of the sixteen USEPA priority PAH pollutants

PAH	Acute[a] Toxicity	Chronic[b] Toxicity	PAH mixture (LC_{50})	Carcinogenic Potency[c]
Naphthalene	4,870	970	71	NA
Acenaphthylene	1181	180	15	NA
Acenapthene	1360	270	23	NA
Fluorene	730	150	90	NA
Phenanthrene	367	55	155	3
Anthracene	300	60	114	3
Fluoranthene	55	11	371	3
Pyrene	61	12	481	3
Benz[a]anthracene	9.8	2.0	111	3
Chrysene	11	2.2	169	3/B2
Benzo[b]fluoranthene	14	2.9	180	2B/B2
Benzo[k]fluoranthene	8.6	1.7	155	2B
Benzo[a]pyrene	7.6	1.5	179	2A/B2
Indeno[1,2,3-cd]pyrene	0.64	0.13	NG	2B/B2
Dibenz[a,h]anthracene	1.3	0.25	NG	2A/B2
Benzo[ghi]perylene	2.4	0.49	NG	3

***a*,b: (Neff et al. 2005); c:(Swartz. 1999) d: (Manoli et al. 1999) NA: No available evidence for human carcinogenicity; 2A/B2: Probably carcinogenic to humans/Probable human carcinogen; 2B: Possibly carcinogenic to humans; 3: Not classified as to human carcinogen**

The application of SQGs in sediment quality analysis has resulted in the development of different effects threshold criteria that include; the Effects Range-Low (ERL) and Effects Range Median (ERM) values (Long et al. 1995); Threshold Effects Levels (TEL) and the Probable Effects Levels (PEL) (Macdonald et al. 1996). The ERLs and ERMs have since been adapted as Interim SQGs (ISQG-Low and ISQG-High guidelines, respectively) in the Australian and New Zealand

guidelines for fresh and marine water quality (ANZECC) due to the paucity of regional data in Australian sediment toxicity studies (McCready et al. 2000).

a) Biological Threshold (ERL/ERM) Approach

Sediment quality guidelines outlined in (Table 2-4), are based on toxicity on sediment dwelling marine animals and have been developed for total PAH in marine sediments (Long et al. 1998). The ERL and ERM are biological classifications derived from the lower 10th and 50th percentiles of effects data respectively (McCready et al. 2006). ERL and ERM guidelines have been derived for all "priority" PAH compounds except benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3,c-d)pyrene (McCready et al. 2000).

The ERL is the value at which toxicity may begin to be observed in sensitive species while the ERM is the median concentration at which toxic effects are observed. Their use in evaluating the potential biological effects of PAHs in river sediments is categorised in three concentration ranges: (i) current levels which do not exceed the ERL; (ii) levels between the ERL and ERM; (iii) levels exceeding the ERM and observed to have probable effect on benthic biota (Guan et al. 2012). The combination of both the ERL and TEL can be used to predict concentrations below limits where adverse effects on benthic organisms are rarely found. In contrast, the ERM and PEL can be utilised in the representation of concentrations above limits which biological adverse effects are found (Viñas et al. 2010).

Table 2-4: Sediment quality guidelines values for PAHs (ng/g). Adapted from (Liu et al. 2009a)

Compounds	Acronym	ERL	ERM	TEL	PEL
Napthalene	NAP	160	2100	34.6	391
Acenapthene	ACE	16	500	6.71	88.9
Acenaphthylene	ACY	44	640	5.87	128
Fluorene	FLU	19	540	21.2	144
Phenanthrene	PHE	240	1500	86.7	544
Anthracene	ANT	85.3	1100	46.9	245
Fluoranthene	FLT	600	5100	113	1494
Pyrene	PYR	665	2600	153	1398
Benzo(a)anthracene	BaA	261	1600	74.8	693
Chrysene	CHR	384	2800	108	846
Benzo(b)fluoranthene	BbF	320	1880	NA	NA
Benzo(k)fluoranthene	BkF	280	1620	NA	NA
Benzo(a)pyrene	BaP	430	1600	88.8	763
Indeno(1,2,3-c,d)pyrene	IND	-	-	-	-
Dibenz(a,h)anthracene	DBA	63.4	260	6.22	135
Benzo(ghi)perylene	BgP	430	1600	-	-

ERL: effect range low; ERM: effect range median; TEL: threshold effects level; PEL: probable effects level; NA: Not available

The SQGs have been applied in a number of PAH studies. For example, in an ecological study on sediments from the Laizhou Bay (China), Liu et al (2009a) showed that the concentrations of monitored PAHs were below their respective ERM, therefore indicating their low ecological risk in surface sediments. However, a few LPAH such as naphthalene and acenaphthylene were found to have exceeded the ERL/TEL value and were therefore, associated with adverse biological effects at the affected stations. In a recent compilation of large toxicity databases for marine organisms from the Sydney Harbour, Australia, correlation analyses and comparisons were established with the mean SQG quotients or ISQG-High (i.e.

ERM and/or PEL) in order to assess relationships between sediment toxicity and contaminant concentration (McCready et al. 2006).

b) Toxic Equivalency Factor Approach

The toxic equivalency factor (TEF) is used to evaluate the relative toxicity of individual chemical components sharing a common mechanism of action (Bostrom et al. 2002). The significant difference between various TEF schemes has been discussed in details in previous PAH toxicity reports (Macdonald et al. 1996; Long et al. 1998). The TEF of PAHs have been evaluated and expressed as dioxin-like toxicity ratios based on the binding activities of aryl-hydrocarbon receptor (AhR) agonists (Villeneuve et al. 2002; Quiroz et al. 2010).

A number of reports have shown the development of a TEF classification scheme (Table A2-1) that provides a measure for the relative potencies of PAHs based on the estimation of toxicity risk values of PAHs that are less potent than BaP. Among the list of TEFs classification scheme available, the one proposed by Nisbet and LaGoy (1992) best reflects the state of the toxic potency of each individual PAH because it includes volatile PAHs such as naphthalene, acenaphthylene and acenaphthene. The PAH carcinogenic potency can also be estimated by calculating the concentrations of individual carcinogenic PAHs in terms of benzo[a]pyrene equivalent (BaPeq) which is represented as follows:

$$\text{Total } BaP_{eq} = \Sigma_i C_i \text{ x } TEF_i$$

where C_i and TEF_i is the concentration and the corresponding toxic of individual PAH and is the corresponding TEF value of one for BaP (Guo et al. 2011b).

A number of environmental studies have undertaken assessment of PAH mixtures using the toxicity ratio which is expressed as toxic PAH equivalents (TEQ_{PAHs}) (Halek et al. 2008; Guo et al. 2011a; Tian et al. 2013). Chen et al (2012) recently reported the toxic equivalent concentrations TEQ for carcinogenic PAHs from the Kaohsiung Harbour, Taiwan. In a related study, Wang et al (2007) applied the BaP toxic equivalency concentrations ($TEQ_{BaP)}$ in the investigation of PAH concentration in soil. The assessment provided a good relationship between toxic equivalent concentrations based on BaP (TEQ_{BaP}) and dioxin-like toxic equivalent concentrations (TEQ_{TCDD}). The study further considered BaP as a good indicator in assessing the potential toxicity of PAH mixtures in soil. In a recent PAH study on the Brisbane River, TEQs values were used to identify PAH trends between sampling sites. The TEQ trend for each site increased with distance from the river mouth to its upstream reaches and showed no significant differences during sampling periods (Shaw et al. 2004).

2.10. CASE STUDY OF PAHs IN THE SEDIMENTS FROM AUSTRALIAN RIVERS

In the last three decades, a limited number of investigations have examined the occurrence and distribution of PAHs in aquatic sediments across Australia. These

investigations were primarily focused on sites in close proximity to heavily populated, urbanized or industrialised centres such as Brisbane, Gladstone, Melbourne, Sydney and Townsville (Maher et al. 1992). There are now, concerns about the increasing number of urban and industrial activities that potentially discharge toxic effluent into water-sheds surrounding these and other sites (Maher et al. 1992; Brown et al. 1992).

In a previous review, Maher and Aislabie (1992) described the levels of PAH in the near shore marine sediments in major Australian estuaries. They established that the major sources of PAHs were predominantly anthropogenic and then classified the various study locations into three categories. These were highly polluted regional urbanised and industrialised catchments, moderately polluted catchments and pristine catchments. An investigation of PAHs from surface sediments in Sydney Harbour, Australia (McCready et al. 2000) revealed that the abundance of individual PAH compounds and the spatial variation observed for PAH concentration (<100 to 380 000 µg/kg) was consistent with high temperature combustion processes, suggesting pyrogenic sources for the PAHs. Kayal et al. (1990) reported that the occurrence and partitioning behaviour of PAHs in the water column, sediment and biota compartments of the Brisbane River, where the predominance of pyrogenic PAHs (combustion-related) were indicated in sediments.

Recent studies on the Brisbane River and Moreton Bay saw Shaw et al (2004) analyse PAH samples in sediments. The investigation reported relatively moderate concentration levels (<LOD - 720 ng/ g) of PAHs in sediment, with a consistent concentration gradient that was consistent during sampling. Prior to that, Muller et

al, detected marked pollution gradients from point/diffuse sites along the Brisbane River at the Brisbane River. PAHs were detected in river sediments at high concentrations ranging from 920-4100 ng/g (Muller et al. 1999). A similar pollution gradient of <0.1-5600 ng/g from the accumulation of sedimentary PAH in the Georges River, Sydney was reported by Brown et al. (1992) with petroleum products to be the main PAH source in the river. Overall, these studies have shown the occurrence and distribution of PAH in urban water-shed which indicate the influence of anthropogenic activities that could lead to long-term pollution of the aquatic ecosystem. The present study was also conducted to assess the extent of recent PAH contamination in the sediments of the Brisbane River and to apportion them to their potential sources.

2.11. PAH SOURCE IDENTIFICATION METHODS

2.11.1. Diagnostic Ratios of PAHs

Identifying the possible sources of PAHs is very important in understanding their fate in the environment. Hence, diagnostic ratios indicator (PAH molecular marker), which is based on PAH concentration are used to distinguish between combustion and petroleum sources of PAHs (Yunker et al. 2002; Hu et al. 2011). However, this method of identification is constrained to specific PAHs with identical molecular masses and similar environmental fate (Baumard et al. 1998; Yunker et al. 2002; Gilbert et al. 2006), in order to negate differences in PAH physicochemical properties such as water solubility and volatility. Diagnostic ratios of ANT/(ANT + PHE), FLT/(FLT + PYR), BaA/(BaA + CHR) and IND/(IND + BgP) using PAHs with molecular masses 178, 202, 228, and 276 respectively have been explored. A

limitation to this PAH identification method is influenced by its qualitative nature and lack of reliability when applied as tracers for PAH source discrimination (Yunker et al. 2002). The diagnostic ratios and their typically reported values for particular processes are highlighted on Table 2-5.

Table 2-5: Typical Diagnostic PAH ratio indicators

PAH ratios	Value Range	Source	References
ANT/(ANT+PHE)	< 0.1	Petrogenic	(Yunker et al. 2002; Gilbert et al. 2006)
	>0.1	Pyrogenic	
FLT/(FLT+PYR)	<0.4	Petrogenic	(Wang et al. 2010; Tobiszewski et al. 2012)
	0.4-0.5	Fossil fuel combustion	
	> 0.5	Grass, wood, coal combustion	
BaA/(BaA+CHR)	< 0.2	Petrogenic	(Soclo et al. 2000; Yunker et al. 2002)
	0.2-0.35	Petrogenic or Pyrogenic	
	> 0.35	Pyrogenic	
IND/(IND+BgP)	<0.2	Petrogenic	(Yunker et al. 2002)
	0.2 - 0.5	Petroleum combustion	
	> 0.5	Grass, wood, coal combustion	

2.11.2. Hierarchical Cluster Analysis (HCA)

Cluster analysis is an unsupervised pattern recognition or exploratory multivariate technique used to classify objects into clusters on the basis that each object is similar to the others within its class but different from those in the other class (Kavouras et

al. 2001; Kannel et al. 2007). It also uncovers intrinsic structure or underlying patterns in a data-set without making a priori assumption. (i.e., membership of all objects and the number of possible groups are unknown). Clusters are also defined through their Euclidean distances which usually serve as a measure of similarity between measured objects (e.g. sampling sites) (Singh et al. 2005).

The application of an appropriate linkage algorithm (single, average, centroid linkage, ward's linkage etc.) is used in linking a group (cluster) of objects with similar distances which are separated by a connector line and represented on a dendogram (tree diagram). HCA has been mainly applied in environmental studies to classify ecological objects such as in the determining of similarities between polluted environmental locations (Simeonova et al. 2006).

2.11.3. Principal Component Analysis (PCA)

PCA complements the application of the classic univariate statistical techniques and provides a powerful tool for elucidation of patterns. PCA is also regarded as a common multivariate data technique that assists in data reduction by transforming an original data matrix into a set of orthogonal latent variables simply referred to as principal components (PCs). A major advantage of the application of PCA for multivariate data analysis is that most of the variability in a data matrix is incorporated into the first two principal components. Each PC is made up of coordinates of either objects or variables, otherwise called the scores and loadings plot, when the objects and variables are being plotted (Lim. 2007). The scores plot allows the comparison of objects with respect to several variables while the loadings

plot is known as the plot of the contribution of the original variables (i.e. pollutants) in other to define a new coordinate system. The positions of the variables in the loadings plot indicate their effect on the arrangement of objects in the principal components plot. Furthermore, it also shows that variables that are plotted close to each other on the loadings plot may be correlated with each other. In general, PCA allows the description of all variables and their effect in relation to the objects. The computation of PCs is undertaken as linear combinations of the original PCs as shown in equation 1:

$$PC_{jk} = a_{j1}x_{k1} + aj2x_{k2} + ... + a_{jn}\, x_{kn} \quad \text{(Equation 1)} \text{ (Lim. 2007)}$$

Where, $PC_{jk} =$ principal component j for object K

$a_{j1} =$ weight coefficient of variable 1 on component j

$x_{k1} =$ the measurement value obtained for variable 1 on object k

$n =$ total number of original variables

The scores and loadings may have positive and negative values for objects and variables, and can be displayed together in a biplot. PCs are chosen such that the first PC explains the maximum amount of variance in a dataset, while the remaining variations are represented by subsequent PCs (Lim et al. 2005). Scores and loadings plots indicate relationships between objects or variables and may be a useful tool for the recognition and elucidation of patterns of contaminants in environmental samples.

$$X = T.\ P + E \quad \text{(Equation 2) (Lim. 2007)}$$

Where X, represents the multidimensional data in a two-dimensional space

T, represents scores

P, represents loadings

E, represents the residuals of matrix X

PCA is the most extensively used multivariate technique for the analysis of complex environmental samples (Mostert et al. 2010). The application of PCA in aiding with chemical analysis helps to identify the contaminant sources and distribution, thereby assisting in site characterisation (Thavamani et al. 2012). However, application of PCA to environmental datasets has some limitations including the absence of physically plausible solutions without recourse to the varimax rotation technique. Additionally, the final solutions produced by PCA are not proportional to actual PAH source contributions (Friend et al. 2011). In other words, PCA cannot be used for properly apportion contaminant sources. In order to carry-out accurate PAH source identification and apportionment, PCA is coupled with multiple linear regression analysis (MLR) otherwise referred to as the absolute principal component scores (APCS), to provide quantitative analysis (Guo et al. 2004; Mostert et al. 2010).

2.11.4. Receptor Modelling Approach

Receptor models are mathematical or statistical procedures used in the identification and quantification of the source of pollutants at a receptor location. The models are applied by assessing contaminant source profiles and contribution in absolute

concentrations, facilitating the validation of the model results by comparison with literature data (Guo et al. 2004). The receptor modelling approach is subsequently based on an assumption that total concentration of each contaminant is made up of the linear sum of its contributions from each of the source components collected at the receptor site (Thurston et al. 1985; Guo et al. 2004). As a result, obtaining a data set for receptor modelling involves determining a large number of chemical constituents such as PAH concentrations in a number of samples (Hopke et al. 2006). However, limitations have been shown towards the use of receptor models. This may be in the form of loss of chemical species during transport from their sources to potential receptor site through the process of chemical and photochemical degradation (Li et al. 2003).

Common receptor models that have been developed include: principal component analysis-absolute principal component scores (PCA/APCS (Thurston et al. 1985), positive matrix factorization (PMF) (Hopke. 2003) and UNMIX (Henry. 2003) These are commonly used multivariate models for the identification of sources and estimating the quantitative contributions of a specific pollutant such as the PAH based on an environmental dataset (Yang et al. 2013). Receptor-oriented source apportionment models have been used for environmental source apportionment in air (Larsen et al. 2003; Singh et al. 2005; Friend et al. 2011), soil (Mostert. 2008; Yang et al. 2013) and sediments (Sofowote et al. 2008; Zhang et al. 2012). For example, PCA-APCS and PMF have been employed for the source apportionment of PAH in soil and sediments (Sofowote et al. 2008; Zhang et al. 2012; Yang et al. 2013), while the UNMIX and PMF are widely applied for source apportionment of ambient

particulate matter and semi volatile organic compounds in air (Engel-Cox et al. 2007; Henry et al. 2010).

The general receptor model can be described on the basis of the index notation shown in equation 3:

$$X_{ij} = \Sigma\, g_{ik} f_{kj} + eij \quad \text{(Equation 3)}$$

Where: Xij is the concentration of species j measured on sample I; p is the number of factors contributing to the samples; f_{kj} is the concentration of species j in factor profile k; g_{ik} is the relative contribution of factor k to sample I; eij represents the error while 'p' represents the total number of factors (Hopke. 2003; Reff et al. 2007).

In the current study, PCA/APCS and PMF were selected as they require no input data on source characteristics, but generate quantitative information on source profile and source strength in terms of absolute concentrations, which enables the model hypothesis to be validated by comparison with estimated source profiles from literature data (Singh et al. 2005).

a) Source Apportionment by PCA-APCS

The Principal component Analysis/Absolute Principal Component Scores (PCA-APCS) is a receptor modelling tool that employs mathematical algorithms including factor analysis (FA), varimax rotation and multi-linear regression for source apportionment studies (Singh et al. 2008; Mostert et al. 2010). It is also referred to as

the stepwise multivariate linear regression integrated principal components analysis (Zhang et al. 2011).

PCA-APCS model subsequently addresses the problem related to PCA by defining an absolute scale for a factor score matrix by the introduction of a true zero value for each factor score calculated by creating an artificial sample with values of zero for each of the variables. The absolute factor scores obtained are used as independent variables while multiple linear regressions are performed using the concentration of PAH as dependent variables in accordance with equation 4:

$$C_i = (bi)_o + \Sigma\, b_{pi}\ APCS_p \quad \text{(Equation 4)}$$

Where p = 1, 2, …., n, $(bi)_0$ is the constant term of multiple regression for PAH and represents the average contribution of the PAH from sources that were not determined by the principal component analysis, b_{pi} is the multiple linear regression coefficient for the source p on variable i, $APCS_p$ is the absolute principal component score of the rotated factor p for a sample, $APCS_p$ x b_{pi} represents the contribution of source p to $C_{i..}$The values of Ci, bi_o and bpi have the same dimensions as the original concentration of the PAH (Ong et al. 2007; Mostert et al. 2010). The number of factors is chosen based on the percentage variance that is explained by each PC obtained from the factor analysis. Varimax rotation separates the variables (chemical species) into source categories or factors, with each factor represented by few variables, which identify the sources of pollution (Mostert. 2008).

The theoretical aspects of the PCA-APCS are complex. Nevertheless, it is simple to perform, as it requires only principal component analysis and multiple linear

regression procedures that are readily available on standard statistical software packages (Guo et al. 2004; Mostert. 2008). Another advantage of the model is that it requires minimum inputs regarding source characteristics in order to provide quantitative information regarding both source profiles (Thurston et al. 1985; Guo et al. 2004). A major disadvantage of the model is that factor loadings derived from PCA-APCS always contain negative values (Chen et al. 2013), which are physically unreasonable during source apportionment in environmental studies. The PCA-APCS receptor model has been successfully applied for the identification and source apportionment of PAH in air (Guo et al. 2004; Singh et al. 2008), aquatic system (Sun et al. 2012), and soil (Mostert et al. 2010; Yang et al. 2013).

b) Source Apportionment by PMF

Positive matrix factorization (PMF) was developed by Paatero and is a widely applied receptor modelling technique that uses a factorisation methodology (Paatero et al. 1993) that has been successfully implemented by the US Environmental Protection Agency among others for multivariate evaluation and subsequent modelling of environmental data sets in order to determine contaminant source profiles and contributions. It is defined as a weighted least squares fit of a data matrix in which the weights are determined depending on the experimental uncertainty (error) estimates of individual data value. PMF models a data matrix as a 2-dimensional factor analytic model expressed by the relationship described in equation 5:

$$X = GF+E \quad \text{(Equation 5)}$$

The model is applied to solve an initial n x m data matrix X (n measurements and m elements) which is factorised into the left and right factor matrices G (n x p) and F (p x m), as well as the 'residual matrix' E (n x m), seen as the unexplained part of X (Vaccaro et al. 2007). The elements of G and F are constrained to have non-negative values in order to have physically meaningful solutions (Sara et al. 2009). PMF is fitted to minimise Q as defined in equation 6:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij}/\sigma_{ij})^2 \quad \text{(Equation 6)}$$

Where:, σ_{ij} is the "uncertainty" in the jth species concentration in sample I;, while m represents the number of species and n is the number of samples. The data matrix X is factored into its components, the factor loading matrix G (source contribution) and the factor score matrix F (source profile). In addition, m, n, and p represent the number of variables, samples, and sources, respectively. The objective function to be minimised is a weighted sum of squares of differences between the measured and calculated elements of the data matrix (Bzdusek et al. 2005).

PMF procedure is classified into three steps: (i) data preparation and processing by the appropriate PMF algorithm, (ii) development of a robust solution, and (c) interpretation of solution obtained (Reff et al. 2007). A major advantage of PMF arises from the fact that it is a posteriori technique requiring no knowledge of source emission profile prior to source apportionment (Vaccaro et al. 2007). It also involves the application of same weight for its measurements, thereby eliminating the bias of

high concentration measurements. Additionally, the model makes use of all available data input, therefore permitting better treatment of missing data and measurements below the detection limit, but requires information on uncertainties in the measurements of pollutant loads, as it shows the quality and reliability of each investigated data point.

Limitation to the use of the model include: information requirement for current and existing source profiles in order to verify the representativeness of the calculated source profiles, dependence of the model on a variety of parameters during set-up and lastly, the requirement of a large amount of data matrix prior modelling. PMF has been applied for PAH source apportionment in environmental matrices.

2.12. MULTICRITERIA DECISION MAKING METHOD

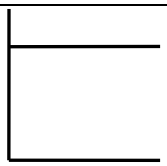
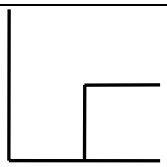
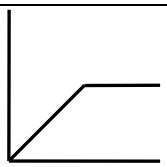
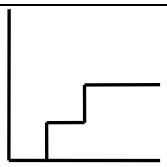
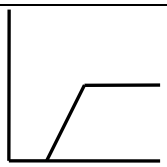
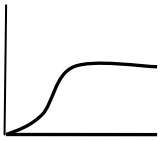
The complex nature of environmental samples such as sediments creates difficulty in inter site comparison especially with the use of univariate statistical methods. However, with the aid of multivariate approaches such as multi-criteria decision making methods, the relationship between this complex dataset are fully explored by the use of non-parametric programs for ranking and integrating complex datasets. Several MCDM techniques, such as simple multi-attribute ranking technique (SMART), preference ranking organisation method for enrichment evaluation (PROMETHEE), analytical hierarchy process (AHP) are available for the purpose of ranking. However, the PROMETHEE program and GAIA has been reported to be the MCDM best suited for environmental applications (Mostert et al. 2010; Friend et al. 2011).

2.12.1. PROMETHEE Analysis

The Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE) is a non-parametric ranking method that facilitates the ranking of a number of objects or actions. PROMETHEE basically involves several steps in solving decision making problems using a series of alternatives (objects), which are compared in pairs and ranked on the basis of the criteria (variables). Each of the objects is assigned a number between 0 and 1 in order to estimate the separation between them.

PROMETHEE facilitates the use of modelling options that shows how an object is ranked and decomposes the outcome relative to another. It measures the deviation between the objects on a single parameter into a preference degree. Consequently, smaller and larger deviations will contribute to a weaker and stronger degree of preference, respectively (Herngren et al. 2006; Ayoko et al. 2007). The preference functions used in PROMETHEE are represented by shapes which are dependent on three threshold values: Q threshold (indifference threshold) known to represent the largest deviation considered to be negligible; a P threshold (preference threshold) which represents the smallest deviation considered to be decisive between two objects and the S threshold (Gaussian threshold) which represents a middle value used only for the Gaussian preference function. The preference functions available for PROMETHEE are highlighted on Table 2-6

Table 2-6: Preference functions in PROMETHEE (Khalil et al. 2004)[1]

Function	Shape	Threshold
Usual		No threshold
U-Shaped		Q threshold
V-shaped		P threshold
Level		Q and P thresholds
Linear		Q and P thresholds
Gaussian		S threshold

Another characteristics of the PROMETHEE model is the refining of the preference selection process with the use of preference flows that compare and rank objects. A positive preference flow (Φ+) expresses the degree to which an object is preferred or outranks other objects, while a negative preference flow (Φ-) expresses the degree to which an object is outranked by all the other objects. The difference between the positive and negative preference flows [net flow (Φ)], is used to rank objects in such

[1] "Reprinted from Analytica Chimica Acta, Vol 506/1, Wael Al-Shiekh Khalil,Ashantha Goonetilleke,Serge Kokot,Steven Carroll, Use of chemometrics methods and multicriteria decision-making for site selection for sustainable on-site sewage effluent disposal. Pages 41-56, Copyright (2004), with permission from Elsevier

a way that the larger the net flow obtained, the higher their ranking order relative to the objects preceding them (Ayoko et al. 2007).

The partial pre-order is observed to produce partial ranking of objects and commonly referred to as PROMETHEE I. This may indicate the following possible outcomes: (a) an object may be outranked by another; (b) two or more objects are indifferent or (c) all objects are incomparable (Lim. 2007). However, the use of this ranking model becomes complex and difficult to interpret when large numbers of objects are involved. Therefore, a second ranking model (PROMETHEE II), that gives a complete ranking of all the objects based on their respective net outranking flow is produced (Mostert. 2008). In this thesis, PROMETHEE II was chosen in order to remove the incomparability between objects of interest as it offers a simpler outcome when compared to PROMETHEE I.

2.12.2. GAIA Analysis

The Geometrical Analysis for Interactive Assistance (GAIA) is a special type of Principal Component Analysis (PCA) in which PROMETHEE results are visualised and displayed as biplots (Ayoko et al. 2007). GAIA produces a GAIA plane defined by the corresponding unit eigenvectors "*u* and *v"*, resulting from a unicriterion net flows covariance matrix. Therefore, GAIA results are based on the positions of criterion (variables) in the GAIA plane and positions of alternatives (objects) in order to determine the strength and weakness of the criterion obtained (Nikolic et al. 2011).

The GAIA plane corresponds to the projection of PROMETHEE results on the first two orthogonal principal components that represent criteria or variables by vectors, whose orientation and length in the direction of a decision axis (π), illustrates their importance. The vectors oriented in similar directions correspond to variables that are in general agreement and the length of the variable vector shows the amount of variance observed. In this case, a variable with a larger variance will have a longer vector than a variable with a small variance (Herngren et al. 2006). The major difference between the PROMETHEE/GAIA method and other multivariate statistical method such as PCA is shown on Table 2-8.

Table 2-8: Comparison between PCA and MCDM. Adapted from (Mostert et al. 2010)

PCA	MCDM
Large and complex datasets can be analysed	Only data matrix consisting of moderate numbers of objects and variables can be analysed
Data pre-treatment is required before data reduction occurs	Data pre-treatment is not required, since PROMETHEE pre-treats the data prior to GAIA
Two or more significant principal components (PCs) can be used to represent the data	Only two principal components (PC 1 and PC 2), are used and displayed as a GAIA plane
Does not use a decision axis (π) in the selection of objects	Has a global decision axis (π), to guide in the selection of the most preferred objects

CHAPTER 3: METHODOLOGY

3.1. SEDIMENT SAMPLING

A sampling plan was designed to include the collection of surface sediment samples from near shore locations centered within two focal points on the river, namely: the urbanised and industrialised zones of the river. With the aid of a global positioning system device (Garmin Global Positioning System; GPS), fifteen sampling sites were chosen taking into consideration the increasing events of land-use that have dominated the river's shoreline which ranged from high-density commercial/Industrial to highly residential/suburban residential areas. The sites were also chosen in order to maximise spatial variation during sample collection from a wide area. Minor deviations from actual sampling sites were also allowed depending on field conditions such as weather conditions, dredging and shipping activities.

The operational area covered Latitude 27°28'49.15"S to 27°23'1.39"S and Longitude 153° 1'40.37"E to 153° 8'37.23"E (Table 3-1). The sampling sites comprised of S-01 and S-02, located in close proximity to a wastewater treatment plant and the Port of Brisbane at the river mouth. Similarly, sampling sites S03-S09 were located in the industrial section of the river. The industries included petroleum refineries, paper recycling plant, sewage treatment plant, fertilizer and cement facilities. However, locations S10-S15 were situated towards the river's upstream reaches and were comprised of a predominantly large urbanised area including the city's central business district. Locations were selected by taking into consideration the increasing land-use that dominates the river's shoreline.

Table 3-1. Description of sampling sites and their GPS coordinates

Site ID	Latitude (S)	Longitude (E)	Site Location	Site Description
S01	27°23'1.39"	153° 9'19.55"	Fisherman's Island	Highly Industrialised. Wastewater treatment plant.
S02	27°23'34.17"	153° 9'25.10"	Port of Brisbane	Highly Industrialised, Port activities and coal storage
S03	27°24'15.03"	153° 9'13.04"	Pinkenba Industrial zone 1	Highly Industrialised, Petrochemical industries
S04	27°24'45.70"	153° 8'37.23"	Gibson Island/ Pinkenba Industrial zone 2	Highly Industrialised: Sewage works, recycling industry
S05	27°25'37.01"	153° 7'50.89"	Bulimba Creek	Moderately Industrialised: Boat building and repair yards, marine fuel stations
S06	27°25'56.20"	153° 7'44.00"	Aquarium Passage	Moderately Industrialised: Agro chemical industry, Marina and boat building and repair yards,
S07	27°26'9.74"	153° 7'6.42"	Gateway Bridge	Motor highway and boat building yards
S08	27°26'49.03"	153° 6'0.54"	Eagle Farm (1)	Moderately Industrialised: Chemical storage, loading docks, wharves, construction sites and parklands
S09	27°26'53.59"	153° 5'38.21"	Eagle Farm (2)	Moderately Industrialised: Ship building and repair yard, ferry terminal
S10	27°26'42.00"	153° 4'50.33"	Bretts Wharf	Highly Residential: Ferry terminal, residential and commercial activities, ferry terminal, marinas
S11	27°26'40.24"	153° 4'11.43"	Breakfast Creek	Highly Residential and commercial, parklands, marinas
S12	27°26'29.43"	153° 2'53.41"	New Farm	Highly Residential and commercial, parklands
S13	27°27'46.08"	153° 2'11.14"	Kangaroo point	Highly Residential and commercial, parklands, marinas
S14	27°28'22.52"	153° 2'1.65"	South Brisbane	Highly Residential and commercial, parklands
S15	27°28'49.15"	153° 1'40.37"	St Lucia/Toowong	Highly Residential, parklands

Surface sediment samples were collected from the selected sampling locations (Table 3-1) on a bimonthly basis in the months of February, April, June, August, and October, 2012. Additionally, due to the wide distance of the study area, sediment samples were collected on two successive days in each month. Sampling was mainly conducted during the low tide to minimize disturbances from high water current in order to maintain the integrity of the sample. A stratified random sampling approach was used to select sampling points, whereby sediment samples were collected randomly and combined into a single sample for each sampling site, in order to provide an unbiased assessment of the condition of the sediment samples. A Ponar stainless-steel grab sampler (Envco, Auckland) (See Figure 3-1), designed to avoid losses during sampling was manually deployed from a fishing boat to obtain surface sediment samples with a maximum penetration of about 5cm. The use of this sampler was also necessary because of the heterogeneous nature of sediments in large urban watershed that was typical of the study area.

A total of 225 individual grab samples corresponding to 3 grab samples from each site location, collected from depths ranging from 1-6 m were amassed throughout the sampling period. The sampling vessel was also moved up to 5–10 m between grabs in the same sampling location in order to ascertain a representative sampling profile. After retrieving the grab samples, they were emptied into a dichloromethane-washed stainless steel bowl. An acetone-rinsed stainless steel spoon was used to scoop the grab sediments samples from the top 1-5cm section sediment for chemical and physical analysis. Finally, the collected samples were transferred directly into clean labelled 250 mL amber glass jars and kept in an ice-cooled esky prior to transport to

the laboratory to minimise loss of contaminant due to volatilization and for homogenisation into composite samples.

Sediment sampling quality control measures using field blank samples for background contamination check of samples was strictly adhered to during sampling. In addition, the sampling equipment was always thoroughly washed after sampling from each site to prevent cross-contamination between sediment samples.

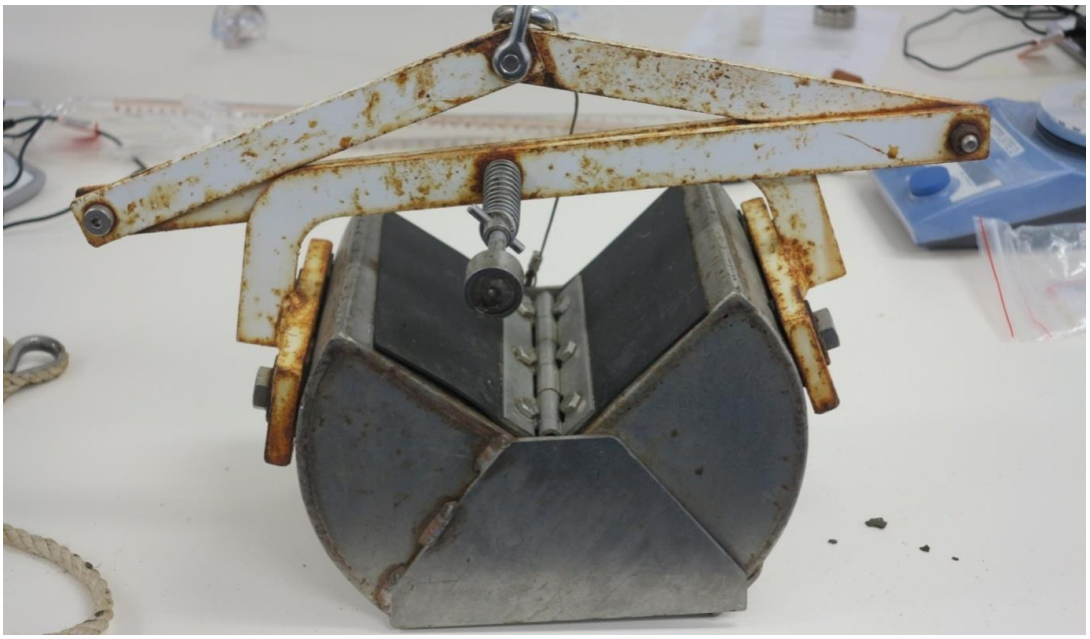


Figure 3-1: The Ponar grab sampler used for sediment sampling (Photograph by Kenneth Ogogo)

3.2. SAMPLE PRESERVATION AND STORAGE

Sample storage conditions and holding times followed standard operating procedures. In the laboratory, 100g of individual grab samples from each sampling sites were carefully homogenized into composite samples with the removal of artefacts such as leaves, twigs, rocks and shells prior to storage in the refrigerator at -20°C. The frozen composite samples were lyophilised with the aid of a freeze dryer

(Virtis Sentry, United Kingdom), that combined high performance refrigeration and vacuum systems at (-50°C) in order to remove moisture and reduce the loss of semi-volatile analytes present in the sample. The freeze-dryer was also checked against possible contamination from back-streaming of oil vapours from the vacuum pump by lodging a blank sample of pure sand (Chem Supply, Australia) through the freeze-drying and analytical procedures.

3.3. ANALYTICAL PROCEDURES

3.3.1. Reagents

Reagents used for chemical analysis were of analytical grade. A certified reference material (CRM) (QTM PAH Mix standard in methylene chloride, 2000 µg/ml) comprised of sixteen USEPA priority pollutants which include: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b+k)fluoranthene B(b+k)F, benzo(a)pyrene (BaP), inde (1,2,3)pyrene (Ind), dibenz(a,h)anthracene (Dba) and benzo(g,h,i)perylene (BgP) and an alkylated PAH (2-bromonaphthalene) was obtained from Sigma Aldrich Chemical Co. Inc. USA. The CRM was used for method optimisation during the preparation of GC-MS calibration curves. It was prepared by dilution with dichloromethane (Chem-Supply, Australia).

Quantification was performed by the internal standard method. A deuterated internal standard solution (semi-volatile internal standard PAH mix in methylene chloride; 2000µg/ml) containing (Napthalene-d_8, Acenapthene-d_{10}, Phenanthrene-d_{10},

Chrysene-d_{12}, and Perylene-d_{12}), purchased from Sigma Aldrich Chemical Co. Inc. USA and a recovery standard (Anthracene d_{-10} in methylene chloride; 2000µg/ml) used for recovery procedures was also purchased from Sigma Aldrich Chemicals. Co. Inc. USA. A standard reference material (SRM) (Organics in Marine Sediment), was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). All standards were preserved in the refrigerator at $4^{\circ}C$ until required.

Organic solvents used in the analytical procedures include: dichloromethane (DCM) acetone and n-hexane purchased from Chem-Supply, Australia and these were stored in amber glass bottles until required. Other reagents include hydrochloric acid (32%), Anhydrous Sodium Sulphate, Silica gel (230-400 mesh ASTM, column chromatography grade) and Alumina-0.063-0.200 mm (basic) supplied by Merck, Australia, copper powder (purchased from BDH laboratory supplies, England), sodium hexametaphosphate $(NaPO_3)_x$ and laboratory sand (Chem-Supply, Australia) anti-bumping granules, diatomaceous earth (Dionex ASE grade), Cellulose filter paper (30mm-Dionex) used in the extraction cell. Ultra-high purity helium and nitrogen were obtained from BOC (Brisbane, Australia).

3.3.2. Preparation of Reagents

A primary PAH working standard solution (10 µg/ml) was prepared by taking 50 µl from the original stock PAH standard mixture (2000 µg/ml) into a 10 mL volumetric flask. Likewise, a working internal standard solution (50 µg/ml) and surrogate standard (10 µg/ml) were prepared from a PAH internal standard mix (2000 µg/ml)

and the recovery standard solution (2000 µg/ml). Six (6) calibration standards were prepared in dichloromethane spanning the range of 0.01-5 µg/ml with the internal standard present at a constant concentration of 2 µg/ml. Dichloromethane was chosen as solvent due to its non-polar characteristics, its capability to extract PAHs, and its easy removal during pre-concentration procedures. In general, the preparation of all laboratory standard solution were undertaken in µg/ml (parts per million; ppm).

3.4. OTHER REAGENTS

Alumina (80-120 mesh) was activated at 450°C for 4 hours while Silica gel was activated at 170°C for at least 24 hours. They were both deactivated with 10% MilliQwater to help reduce their adsorption capacity and improve their reproducibility. Granular anhydrous Sodium Sulphate (Na_2SO_4, analytical grade) was baked at 450°C for 2 hours, while glass wool was also pre-conditioned at 120°C for 24 hours. They were also stored in a sealed desiccator prior to use. Copper powder was activated using concentrated hydrochloric acid (HCL;32%), followed by exhaustive rinses with milliQwater and acetone, dried in the oven and stored in a desiccator prior to use in the removal of sulphur from the sample matrix.

3.5. SAMPLE PRE-TREATMENT

Sample pre-treatment was carried out on dry and wet sediment samples for the analysis of sediment physicochemical parameters such as electrical conductivity (EC), acidity and alkalinity (pH), organic matter and water content. Sample pre-

treatment was also performed on sediment samples to increase the homogeneity and extractability of the analytes in sediments during chemical analysis.

3.5.1. Determination of pH and EC

Analyses were performed for pH and EC by a modification of methods (4AI and 3A) of 1:5 soil/water (w/v) suspension from the Australasia soil chemical methods (Rayment and Lyons, 2011) The pH and electrical conductivity were both measured as sediment-water slurries that were equilibrated under controlled conditions using a portable pH–EC meter (Accumet Excel XL60, Fisher Scientific Inc., USA), which was calibrated using the pH buffer solutions (4.00, 6.86, and 9.18) at 25 0C prior to measurements. The procedure was carried out by weighing out 10 g of dried sediments and placing it in a 100 mL Nalgene tube containing 50 mL distilled water. The mixture was placed on a mechanical shaker for 2 hours and allowed to settle for 30 minutes prior to pH and EC measurement on the supernatants.

3.5.2. Determination of Sediment Organic Matter

Organic matter content is the percentage of mass of organic matter in a dry sediment sample. It was determined using the combustion of organic matter and Loss on Ignition method (LOI) (Matthiessen et al. 2005). A crucible with the dried sediment was placed in a muffle furnace at a temperature of 550˚C for 5 hours to combust the organic matter present and left to cool in a desiccator at room temperature, the crucible was re-weighed to determine the mass of the crucible and the ash. The

difference in mass was used to determine the amount of organic matter in the sediment as shown by the equation below:

LOI_{550}= [$Mass_{105}$-$Mass_{550}$/$Mass_{105}$] x 100

Where: LOI_{550} represents LOI at 550^0C (%)

$Mass_{105}$ represents dry weight of sample before combustion

$Mass_{550}$ represents dry weight of sample after combustion at 550^0C

3.5.3. Determination of total organic carbon (TOC)

TOC in the sediments was determined using method 6B3 from the Australasia soil chemical methods (Rayment and Lyons, 2011) and involved the direct acidification of sediment sub-sample to remove carbonate prior to the determination of organic carbon in the sample. It generally involved using freeze-dried sediment (~ 0.5 g) placed in a combustion boat (528-203) containing a Nickel liner (502-343) and treated by direct acidification with 5-10 drops (4M HCL), sufficiently covering the sample. Samples were dried at 60 °C (Rowe scientific series 2000) for 24 hours and allowed to cool in a desiccator prior to TOC determination on an Elemental Analyser (LECO TruMac series, Michigan, USA). Quality control measures were also applied throughout the combustion process with empty nickel liner and combustion boats that were ran before and after each analysis Samples were analysed in duplicate and the standard deviations were less than 5 %. Ethylenediaminetetraacetic acid (EDTA) was used as a reference standard to verify the calibration of the instrument, Precision was ± 3.9% for TOC based on the coefficient of variation of replicate analysis (n = 10) of a reference standard). Marine sediment standard (NIST 1941b) was also analysed on a dry weight basis for the validation of the TOC procedure.

3.5.4. Grain Size Distribution

Particle size analysis was determined as sediment grain size distribution, using a laser diffraction method on a particle size mastersizer (Malvern Mastersizer/S, Malvern instruments; Worcestershire, UK) (Figure 3-2). The method was considered based on specific criteria that include available sediment quantity, measurement speed, efficient data processing, and reproducibility of the results. The Mastersizer consists of a reverse 300mm Fourier lens able to analyse particle sizes and operational range of 0.05-900µm. The system consists of a sample dispersion unit connected by flow cells to the optical unit. The particle sizes derived from the laser diffraction instrument were expressed as a volume distribution and then converted into a number distribution, whereby particles were made to represent 99.9 % of the total distribution.

3.6. SAMPLE PREPARATION PROCEDURES:

3.6.1. Particle Size Pre-treatment and Analysis

A Malvern mastersizer laser diffractometer was used for grain size distribution analysis. Sediment sub-samples (approximately 10 grams) were placed in individual Nalgene tubes, with each sample immersed in acetic acid for carbonate removal and allowed to sit for 24 hours in a fume-hood. Upon carbonate removal, samples were digested with 15 mL of 30% hydrogen peroxide for the complete removal of organic matter for 24 hours Sodium hexametaphosphate (NaHMP) (calgon) surfactant solution (50 g/L) was used as a dispersant to move aggregates between samples. Sediment sub-samples (10 g) were subsequently immersed in 10 mL of a NaHMP

solution and mixed overnight using an end-over-end shaker (So et al. 1997). Samples were added into the dispersion unit of the Mastersizer and measured for their particle sizes.

Figure 3-2: Malvern mastersizer laser diffractometer used for grain size distribution analysis (Photograph by Kenneth Ogogo)

The particle size analysis was carried out in triplicate with the data obtained representing the average of the three measurements. The operation on the particle size analyser was controlled by a personal computer.

Particle size analysis using the Malvern Mastersizer was carried as follows:

(a) alignment of the optical lens for a correct detector obscuration

(b) injection of distilled water into the measuring chamber to allow the instrument adjusts the light level and determines the background value automatically

(c) addition of prepared sample into the chamber to allow for dispersion, proper water circulation for the formation of the suspensions used for the measurements particle sizes

(d) a rinse of the dispersion unit prior to subsequent sample run

3.6.2. Accelerated Extraction Procedure

An accelerated solvent extraction method extractor (ASE) also termed as pressurised fluid extraction was used for sediment extraction using the accelerated solvent extractor (ASE™ 350, Dionex Corporation, Sunnyvale, CA, USA) which consists of a carousel capable of carrying 24 sample vessels (Figure 3-3). ASE also operates on the principle of high pressure and temperature. The high temperature aids the extraction solvents to effectively solubilise the analytes present in the sample, further accelerating the extraction kinetics while the high pressure is applied to keep the extraction solvent(s) in the liquid state (Braendli et al. 2006).

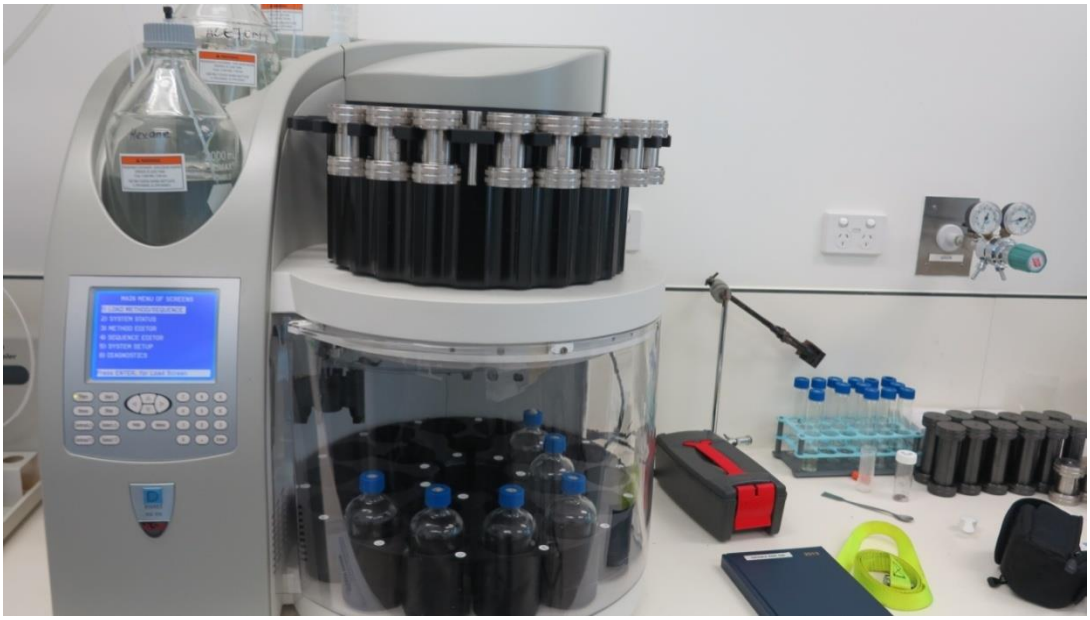


Figure 3-3: Accelerated Solvent Extractor used for sediment extraction (Photograph by Kenneth Ogogo)

Freeze-dried sediments were filtered through a 2-mm sieve to remove artefacts such as gravel, roots, sticks and shells prior to sediment extraction. Sample mass (~10 g) was mixed with an ASE prep-diatomaceous earth (hydromatrix and filler material

that aids in the increase the surface area within the sediment samples) and activated copper powder (1g) in a 33 mL ASE stainless-steel cell which was generally used for extraction. Activated copper powder was added into the extraction cell to remove traces of sulphur in sediment samples. The ASE programme set-up used in the extraction of sediment is outlined on Table 3-2.

Sediment samples were spiked with the recovery standard solution (2 µg anthracene d-10) to monitor recovery rate of the procedure; the solvent mixture used was (DCM:Acetone, 3:1 v/v; 67 mL) (Nikolaou et al. 2009). The ASE static extraction step was repeated twice (2 cycles) and rinsed with fresh solvent after the last static step for a total run-time of 17 minutes. At the final step, the samples were purged with nitrogen gas (N_2) in order to recover the last solvent residues. The extracts were collected in a 100 mL pre-cleaned glass vial and further concentrated to 5 mL using a rotary evaporator (Buchi R-210/R-215) under vacuum conditions. The extract was transferred to a glass vial (10 mL) and further concentrated to 2 mL using a stream of nitrogen gas prior to the clean-up procedure.

Table 3-2: ASE operational parameters for PAH extraction in sediment samples

Temperature	**Heat time**	**Static time**	**Cycles**	**Rinse volume**
110^0C	6 mins	5 mins	2	60%
Purge	Solvent A	Solvent B	Cell type	Pressure
60s	Acetone	Dichloromethane	Stainless steel	1500psi

3.6.3. Extract Clean-up and Concentration Procedures

Sample clean-up was carried out for all extracts in order to selectively remove target compounds from the sample matrix, increase the limit of detection (LOD) of target analytes and remove compounds that might interfere with the elution of the target compounds. The clean-up process was carried out using a glass chromatography column (1.3 cm i.d. x 30 cm) and fitted with Teflon stopper. The glass column was filled with 12g slurry of silica gel (mixed with methylene chloride) and an addition of 6g of alumina and finally topped up with a gram of anhydrous sodium sulphate in order to remove traces of water and prevent column dry-out during contact with air; hence improving the performance of the chromatographic analysis. The column was deactivated by eluting with 10 mL n-hexane and the eluate discarded. Further elution was carried out with 25 mL organic solvent mixture of dichloromethane and n-hexane (3:7, v/v) (Hu et al. 2010) to obtain extracts containing target PAH compounds. Extracts were reduced in a rotary evaporator to 3 mL, solvent exchanged with 5 mL of n-hexane and finally blown down to 1 mL under a gentle stream of nitrogen. Extracts, reduced below 0.5 mL were adjusted to 1 mL with the solvent mixture (dichloromethane and n-hexane). The final concentrate was transferred into a GC microvial and stored in a refrigerator prior to analysis.

3.6.4. Instrumental Analysis for PAHs

PAH analysis was carried out on a HP 6890 gas chromatograph fitted with an Agilent HP-5 capillary column with a length of 30 m, an internal diameter of 0.32 mm, a film thickness of 0.25 µm coupled with a mass selective detector (MS 5973)

(Agilent Technologies, Australia) (Figure 3-4). The Mass Spectrometer (MS) was operated in the electron impact mode with ionization energy of 70eV, an electron multiplier voltage of 1,288 eV and mass scanning range of m/z 35-500 at 2 scans per second. The MS ion source and interface were held at 250˚C and 280˚C, respectively, in order to improve the responses and peak shapes especially of the late eluting PAHs, (i.e. higher molecular weight PAH). The GC-MS full scan mode and the selected ion-monitoring (SIM) modes were employed for the tentative identification and quantification of PAH compounds, respectively. Prior to GC-MS analysis, a method optimization for the qualitative and quantitative analysis of PAHs was carried out. It was achieved by a "one-variable-at-a-time approach" and involved the selection of several temperature ramping and gas flow parameters. Surrogate and PAH standards were also used during the optimization of GC-MS parameters to develop the multilevel calibration with six concentration levels (0.01, 0.05, 0.1, 0.5, 1, 5 µg/mL) for the preparation of a linear calibration curve. Identification and quantification were carried out against these linear calibration standards using an internal standard method that was based on the US EPA METHOD 8270D. The correlation coefficient (R^2), showed good linearity which ranged from 0.993 to 0.999 and these were used to determine the concentration of each PAH compound in the extracts value. The peak area for each designated quantification m/z ratio in Table 3-4 was integrated using the ChemStation GC/MS software.

Figure 3-4: Gas Chromatograph and Mass Spectrometer (GC/MS) used for PAH analysis (Photograph by Kenneth Ogogo)

Following injection of a sample extract into the GC column inlet, the column was held at 60˚C for a minute and then ramped at 25˚C/ minute to 150˚C followed by 15˚C/ minute to 190˚C, held for 1 minute, followed by 10˚C/minute to 250˚C, held for 2 minutes and finally ramped at 6˚C/minute to 300˚C where it was finally held for 3 minutes to give a total runtime of 27.56 minutes. The GC operating parameters are outlined in Table 3-3. Selected PAH compounds were identified by their retention time relative to the reference standard and the relative abundance of the monitored ions. The individual PAH peaks were positively identified if they were within ±0.05 minute of the retention time given by the calibration standard. For quantification purpose, the spectral fragmentation patterns from the three most abundant ions for each PAH were monitored using a NIST-2008 mass spectral library as shown in Table 3-4.

Table 3-3: GC-MS operating conditions for qualitative and quantitative PAH analysis

Injector Mode	Splitless
Inlet Temperature	280˚C
Oven Temperature	Initial temp of 60˚C for 1min, 60-300˚C,hold for 3 minute
MS quadrupole Temperature	150˚C
Injection Volume	2 µl (Scan Mode) 1 µl (Sim Mode)
Helium Gas Flow	1.2 ml/minute
Purge Flow	60.1 ml/minute
Purge Time	1.5 minute
Total Flow	64.0 ml/minute
Solvent Delay	3 minutes

For the GC-MS analyses, extracts were spiked with an internal standard mix containing (2 µg) of each of its constituents that was subsequently used for the target PAH quantification and to compensate for the lack of linear response curve by the mass selective detector. Sediment PAH concentrations were calculated by dividing the amounts in extracts by the actual weight of sediment extracted as shown below:

$$\text{PAH concentration (mg/kg)} = \frac{A \times B}{C} \times D_f \times 1000$$

Where, A represents the concentration of PAH in extracted solution, [mg/L]; B represents the final volume of the extract [mL]; C represents the weight of the sample [g]; D_f represents the dilution factor.

Table 3-4: GC-MS condition for PAH under selected ion monitoring (SIM) mode

Compounds	Retention time (mins)	Quantification ions (m/z)	Confirmation ions (m/z)
▪NAP-d_s	4.76	136	68,137
NAP	4.77	128	127, 129
BNAP	6.66	206	127
▪ACE-d_{10}	6.7	164	162, 165
ACY	6.5	152	151, 153
ACE	6.73	153	152, 154
FLU	7.39	166	163, 165
▪PHE-d_{10}	9.02	188	94, 189
PHE	9.04	178	176, 179
*ANTd_{10}	9.1	188	94, 189
ANT	9.14	178	176, 179
FLT	11.63	202	101, 203
PYR	12.1	202	101, 203
▪CHR-d_{12}	15.07	240	120, 241
BAA	15.03	228	226, 229
CHR	15.12	228	226, 229
B[b+k]F	18.47	252	126, 253
BAP	19.46	252	126, 253
▪PER-d_{12}	19.65	264	265
IND	22.86	276	138, 227
DBA	23.01	278	139,279
BGP	23.54	276	138,277

*** Surrogate standard: ANT-d_{10}; ▪ Internal standards: NAP-d_8, ACE-d_{10}, PHE-d_{10}, CHR-d_{12}, PER-d_{12}:**

The analytical quality control measures were carried out regularly to check the integrity of the entire analytical process. Four QA/QC procedures were applied in this study: (a) Laboratory apparatus cleaning, (b) Recovery monitoring, (c) Blanks and detection limits and (d) Analysis of a standard reference material. Stock and

prepared laboratory standards were also checked regularly for signs of deterioration (i.e. discoloration, formation of precipitates and changes in concentration).

a) Laboratory Apparatus Preparation

Glassware was cleaned by washing in detergent, rinsed with distilled water and finally with organic solvents (acetone and dichloromethane). They are dried overnight in an oven (Rowe scientific series 2000) at 100˚C in order to minimize unexpected interference during instrumental analysis. Reagent blanks were prepared to check the cleanliness of the laboratory glassware. Furthermore, components of the extraction cells and collecting vials were ultrasound-cleaned with distilled water followed by acetone and dried inside the oven. GC syringes used for standard preparation were always rinsed with dichloromethane prior to usage.

b) Recovery Procedure applied for PAH Analysis

Prior to extraction procedure, all samples and blanks were spiked with a known amount (2 µg) of deuterated PAH compound (anthracene-d10) in order to monitor the performance of the analytical procedure and determine the extraction recovery for the specific PAHs. The recovery rates for surrogate samples were expressed as the percentage recovery and taken to be the recovery rate of target compounds in the sample. The recovery of 92 ± 14 % was obtained from the surrogate standard, but was not used to correct for reported PAH concentrations. PAH concentration levels were presented on a dry-weight basis. The certified reference material (QTM PAH MIX) with concentration: 0.01µg/g, 0.05µg/g, 0.1µg/g, 0.5µg/g, 1µg/g and 5µg/g was also applied as matrix spike standards in order to determine the percentage PAH recoveries. Blanks were spiked accordingly with a known amount (2 µg) of PAH

calibration standard and analysed with the same procedures as for the samples. PAH recoveries from the samples ranged between 82-115% and were shown to be generally within the U.S. EPA control limit (80%-120%) for PAH in soil/sediment (USEPA. 1994).

c) Blanks and Estimation of Detection Limits for PAH

Laboratory and field blanks were always prepared and analysed in a similar fashion as the samples in order to monitor background contamination during the analytical procedure and to demonstrate the absence of measurable peaks at the retention times of the analytes of interest. Field blanks were analysed in every batch of samples and was subsequently used for blank subtraction of the observed sample concentrations.

Limits of detection were derived from the blanks (n=7), and quantified as three times the standard deviation of the mean PAH concentrations in the blanks (Harris. 2010). When individual PAHs were not detected in blanks (as the case of), LOD were calculated as the mean value of the baseline noise plus three times the standard deviation of this noise. Whereas the method detection limit (MDL) was determined by analysing method blank samples (i.e. taken through the entire analytical process). The LOD and MDL that were applied for the present study are shown in Table 3-5.

Table 3-5: Detection limits for PAH determination

PAH	Abbreviation	Limit of Detection (µg/g)	Method Detection Limit (µg/g)
Naphthalene	NAP	0.0005	0.008
2-bromonaphthalene	BNAP	BDL	0.0002
Acenapthene	ACE	BDL	0.0004
Acenaphthylene	ACY	0.0013	0.0029
Fluorene	FLU	BDL	0.0011
Phenanthrene	PHE	0.0056	0.0103
Anthracene	ANT	BDL	0.0023
Flouranthene	FLT	0.0019	0.01
Pyrene	PYR	0.0034	0.0078
Benzo(a)anthracene	BaA	BDL	0.00108
Chrysene	CHR	BDL	0.0056
Benzo(b+k)fluoranthene	B[b+k]F	0.0022	0.0045
Benzo(a)pyrene	BaP	0.0024	0.0055
Indeno(1,2,3-cd)pyrene	IND	BDL	0.01
Dibenzo(a,h)anthracene	DBA	BDL	0.002
Benzo(g,h,i)perylene	BgP	BDL	0.013

LOD and MDL concentrations measured in µg/g (ppm); BDL=below detection limit

d) Method Validation using Standard Reference Material.

The analytical procedure was validated by analysing a Standard Reference Materials (NIST SRM 1941b- Organics in Marine Sediment) (Wise et al. 2004). 0.5g of SRM marine sediment was introduced into the ASE cell and analysed in replicate (n=3) with the same analytical procedure as applied for sediment samples. Certified values were satisfactorily comparable with measured PAH values, except NAP, ACY, and FLU; as they showed low recoveries (Table 3-6). Low recoveries of these PAHs could be attributed to their physical properties where they represent more volatile

PAH compounds. Good recoveries from other PAHs further affirmed the accuracy of quantification method used for PAHs analysis in this thesis.

Table 3-6: Method validation results using NIST certified reference material

PAH Compounds	Certified value (µg/kg)	Measured value (µg/kg)	CV (%)	Recovery (%)
NAP	848 ± 95	602 ± 42	1.4	70.9
ACY	53.3 ± 6.4	32 ± 4.1	1.7	60
ACE	38.4 ± 5.2	32 ± 2.0	1.2	83
FLU	85 ± 15	62 ± 11	1.4	72.9
PHE	406 ± 44	396 ± 36	1.0	97.5
ANT	184 ± 18	169 ± 12	1.1	91.8
FLT	651 ± 50	639 ± 48	1.0	98
PYR	581 ± 39	592 ± 35	1.0	102
BaA	335 ± 25	311 ± 13	1.1	92.8
CHR	291 ± 31	278 ± 9	1.0	95.5
BbF	453 ± 21	NA	NA	NA
BkF	225 ± 18	202 ± 13	1.1	89.7
BaP	358 ± 17	346 ± 12	1.0	96.6
IND	341 ± 57	321 ± 22	1.1	94
DBA	53 ±10	45 ± 6	1.2	84.9
BgP	307 ± 45	288 ± 26	1.1	93.8

µg/kg (ppb); %CV= Coefficient of Variation; NA (no available data)

3.7. DATA ANALYSIS TECHNIQUES

In order to highlight the relevant patterns and sources of the obtained PAH concentration levels from the sampling locations, statistical approaches based on univariate and multivariate data techniques were utilised. Simple descriptive statistics, which include the mean, median and standard deviations, were calculated using Microsoft Excel 2007 and Sigma Plot version 12.3. Multivariate data analysis performed includes HCA and PCA. Source apportionment techniques using PCA-

APCS, PMF and ranking analysis that include MCDM were chosen for the data analysis.

3.7.1. Hierarchical Cluster Analysis

In this thesis the hierarchical cluster analysis (HCA) was carried out using a between-groups linkage cluster method and a squared Euclidean distance metrics for measuring distances between similar objects applied to detect similarities in PAH contamination in the different sampling sites. HCA was carried out on an IBM SPSS software package.

3.7.2. Principal Component Analysis

PAH data pre-treatment and PCA were conducted on SIMCA 13.0 statistical software package (Umetrics, Sweden). PCA was carried out in order to evaluate as well as classify the resulting principal components according to their significance level. The significant principal components (components having eigenvalues greater than unity) obtained from this study described the largest amounts of variance that determined the data distribution and were designated as R^1 and R^2, while NS is designated as the non-significant principal components. R^2X explains the fraction of the data that is explained by the principal component while R^2 (cum) explains the cumulative fraction of the data as more components are added. In addition, the Q^2 values indicate the predictive ability of the model, with high Q^2 values indicating a positive predictive attribute of the model (Mostert. 2008). SIMCA also applies a 95% hotelling circle/ellipse, highlighting the principal component scores which also

indicate modal class boundaries. Objects falling outside these boundaries are labelled outliers and subsequently removed. However, no outlier was observed in the PCA analysis applied for this study.

3.7.3. PAH Source Apportionment Analysis

Data analysis using the receptor models was carried out on a data matrix consisting of 15 observations (sampling sites) and 16 variables (16 EPA PAHs and an alkylated PAH compound), in order to estimate the source contributions of PAH in sediments.

3.7.3.1. **Source apportionment by PCA-APCS**

For the PCA-APCS model, PCA applying varimax rotation was performed on the dataset. The factor scores from the PCA and the total PAH concentrations were used as independent and dependent variable respectively for a multi-linear regression and as standardised regression coefficients. The absolute principal component scores (APCS) was obtained using the eigenvalue matrix with principal components taken to be significant when they displayed eigenvalues >1) and the principal component score matrix. Finally, multiple linear regression coefficients were used to convert the absolute principal scores component into the mass concentrations to obtain the contribution of the different sources of the total PAH present in the sediment samples. Multiple linear regressions were performed in a stepwise manner to allow for the insertion and removal of tracers to improve the fit of the model. The multiple regression models is represented by equation below:

$$Y=\sum_{i=1}^{p} m_i X_i + b$$

Where: Y is the dependent variable ($\sum_{16}$PAHs), m_i is the modelled regression coefficient, X_i is the concentration of the identified tracer, b is the regression constant and p is the number of identified sources. PCA-APCS was run using an IBM SPSS Software package Version 19 (SPSS Inc., USA) and Microsoft Office Excel 2010 program. A more detailed description of PCA-APCS model outlined in the literature (Thurston et al. 1985; Guo et al. 2004).

3.7.3.2. **Source apportionment by PMF**

The principal difference of PMF compared with the other receptor models is that this model considers the uncertainty of each variable (Yang et al. 2013). Generally, an uncertainty measurement was estimated by using known concentrations, mainly the method detection limit (MDL) for individual PAH. Zero values obtained for PAH concentration were replaced with median values calculated. Similarly, missing values were replaced by the geometric mean concentration of the compound, while a value equal to one half the detection limits was used for concentrations below the detection limit.

The selection of variables and the optimisation of factor numbers for PMF were based on the signal to noise ratio (S/N), along with the convergence between a Q robust (obtained value) and Q true values (theoretical *Q* (number of elements in the data matrix), the distribution of residuals for individual species as well as the scatterplots of the predicted mass versus the experimental mass. The Q values were

used as goodness-of-fit parameters, denoting an assessment of how well the model fit the input data. The Q robust was calculated by excluding outliers, defined as samples for which the scaled residual. An F-peak value was minimised and used to control rotation in the data. As a result, an intermediate choice of F-peak parameter (F-peak = 0) was adopted in the model fitting, implying that Fpeak rotation was not required to improve oblique edges (i.e. unrealistic rotation of a factor). Multiple runs were carried out to improve results by down weighting PAH species with low S/N ratio. The evaluation criteria outlined by (Friend et al. 2011) was used to evaluate the PMF results and determine the optimal solution, which subsequently provided a four-factor PMF solution. PMF analysis was conducted on a USEPA PMF 3.0 software program while the operational procedure was derived using the EPA PMF user guide interface.

a) MCDM Analysis

In the current study, the raw data matrix was analysed based on appropriate modelling options including preference functions, thresholds and weighting assigned to each variable prior to the use of PROMETHEE and GAIA. They were used to rank sediment samples from each sampling location on the basis of a range of variables or criteria (PAH concentrations). The V-shaped preference function using an indifference threshold that allows all alternatives to be compared on a linear basis was subsequently chosen as the preference function. In addition, an equal weighting was assigned to the variables (PAHs) from the study to ensure that the PAH under consideration were attributed the same significance, that is, each of them has a similar effect in the environment and therefore, no variable was favoured over the

other. Furthermore, since the method required that each variable be separately modelled and optimised (that is, either ranked top-down maximised or bottom-up minimised), the concentration of the chemical species were minimised and lower values preferred due to the assumptions that lower concentration values of these variables indicate better sediment quality. MCDM was conducted on a Visual Decision Laboratory software package (Visual decision Inc, Montreal, Canada).

CHAPTER 4: RESULTS & DISCUSSION

4.1. COMPOSITION OF PAHs

Results were obtained for the 16 US EPA priority PAH compounds which include: Naphthalene (NAP), Acenapthalene (ACE), Acenapthylene (ACY), Phenanthrene (PHE), Anthracene (ANT) and Fluorene (FLU), Fluoranthene (FLT), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-c,d)pyrene (IND), Dibenzo (a,h) anthracene (DBA) and benzo(ghi)perylene (BgP). Results were also obtained for an alkylated PAH compound, 2-bromonaphthalene (BNAP). Notably, BbF and BkF were measured as one parameter (B[b+k]F).

The composition and relative abundance of the individual PAHs in all sediment samples is summarised in Figure 4-1. The mixture of PAH present in all samples were qualitatively similar, including those from distant sites. The relative abundance was determined according to the number of aromatic rings namely as: 2-3-ring, 4-ring, and 5-6-ring compounds which may also be represented as low, medium, and high molecular weight PAHs, respectively. A distinct variation in the relative concentrations of low molecular weight PAH compounds (LPAH), defined as $m/z \leq 202$ (2-3ring PAH) and high molecular weight PAH compounds (HPAH), defined as $m/z \geq 202$ (4-6ring PAH) was observed in most of the sampling sites. As expected, the composition of HPAH was shown to be present at higher in concentrations than the LPAH, because HPAH are more hydrophobic in the aquatic environment and are preferentially incorporated in the sediments.

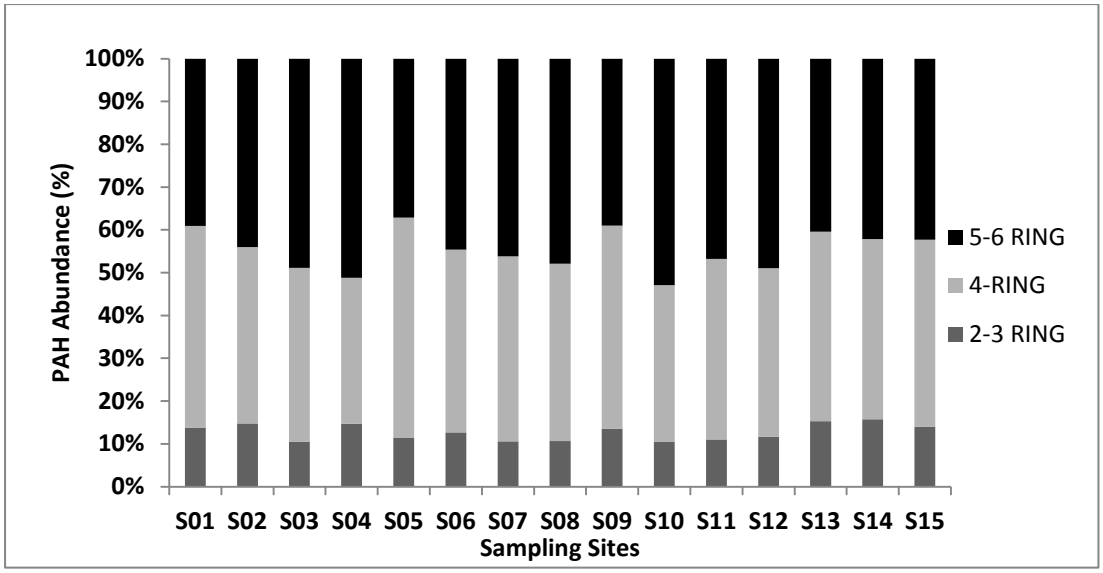


Figure 4-1: Relative PAH (%) abundance across the study sites

Overall, the HPAH dominated the total PAH concentrations, accounting for more than 80% of the total PAHs with the 4-ring and 5- & 6-ring PAH representing 45% and 35% of the total PAHs, respectively. The predominance of HPAHs in the sediments samples reflected the presence of significant combustion products from pyrolytic processes and/or sources. The results were in agreement with a previous study of the Brisbane River (Kayal. 1990) and similar work conducted on PAH distribution at the Sydney Harbour, Australia (McCready et al. 2000). These studies have shown that majority of urban sediments in aquatic environment consists strongly of a pyrogenic PAH composition.

In contrast, the 2–3 ring compounds contributed less than 20% to the PAH compositional profile. This result from the compositional profile further reflected the presence of combustion products from low temperature pyrolytic processes in the study area. The 2–3 ring PAHs exit predominantly in the vapour phase and tend to be less persistent in sediments. Their low concentrations in the sediment samples

have been attributed to environmental processes such as biodegradation during their transportation over long distances in water (Brown et al. 1992).

In summary, the PAH profile was in good agreement with the observation from an earlier PAH study carried out in the Brisbane River by Kayal et al. (1990). The dominance of un-substituted PAHs and the elevated levels recorded for the 4-6 ring PAH, especially the isomeric pairs; FLT and PYR (m/z 202), B[b+k]F (m/z 252), BaP (m/z 252), IND (m/z 276) and BgP (m/z 276), which are typical of combustion generated PAH was noted.

4.2. TEMPORAL TRENDS OF PAHs

A comparison of the PAH concentration levels from the different sampling periods revealed some temporal variations between the individual PAHs in sediments. Higher PAH concentrations were recorded during the late winter (604 ± 510 ng/g) and spring (887 ± 706 ng/g) with relatively lower PAH concentrations observed during summer (523 ± 418 ng/g). Figure 4-2 illustrates the bimonthly trend of PAH concentration across the sampling sites investigated. The notable increase in the average PAH concentrations starting from the sampling period of June through to October (508-768 ng/g) (Table A3-1) also coincided with winter and spring period. It is worthy to note that these seasons are both typically dry periods in South East Queensland.

One-way ANOVA was used to determine the significant difference across the average monthly PAH concentrations. The mean PAH concentrations were not statistically significant ($P > 0.05$) across the assessment period. This implied that there was no pronounced temporal variation in PAH concentration level in the sediment samples collected during the monitoring period.

4.3. SPATIAL DISTRIBUTION OF PAHs

Spatial distribution of PAHs was evaluated by grouping the fifteen sampling sites spanning the study area into two groups: the urban and industrial. The reported PAH concentrations were presented as the total mean PAH concentrations in sediments during the sampling period. PAH concentrations ranged from 334 ng/g (S-01) to 1038 ng/g (S-15) with a mean concentration of 571 ± 203 ng/g.

PAH spatial distribution was observed for the study as shown in Figure 4-2. The highest concentrations was shown to range from 387-1032 ng/g and corresponded to sites S-04 to S11 and S14. These sites were located in the urban and industrial areas along the river, and could be associated with petrochemical storage facilities, industrial (mainly maritime) and commercial activities. This suggested that urbanization contributes to the discharge of contaminants into the river as, evidenced by the fact that the sampling sites (S-04 to S11) were shown to contain measurable amounts of pyrolytic-sourced PAHs which include 3-ring PAH (PHE and ANT) and 4-6 ring PAH (FLT, PYR, BaA, CHR, B[b+k]F, BaP, IND and BgP). In general, the distribution of PAH around these sections was thought to be site specific and the likely influence of contamination could have resulted from the intensive maritime

activities and land traffic emissions. In contrast, the sampling sites S-01, S-02, S-03 and S12, S13, S15, located at the downstream and upstream sections of the river, showed lower PAH concentrations ranging from 319-398 ng/g. The sampling sites in the downstream section were located in close proximity to major industrial facilities such as the petroleum refinery complex, waste-water treatment plant and the port of Brisbane, whereas the upstream sites were predominantly located around residential areas. The low PAH concentrations observed for these sites was in good agreement with previous PAH assessment in the Brisbane River, sediments at the downstream section of the river and, particularly samples that were taken close to the river mouth. The decline of PAH concentrations in sediments from these sites in the lower reaches of the Brisbane River could be attributed to dilution of sediment contaminants as a result of river flushing (Shaw et al. 2004), biodegradation and desorption of low molecular weight PAHs (especially acenaphthylene, acenaphthene and fluorene) from the water surface during transport (Maher et al. 1992).

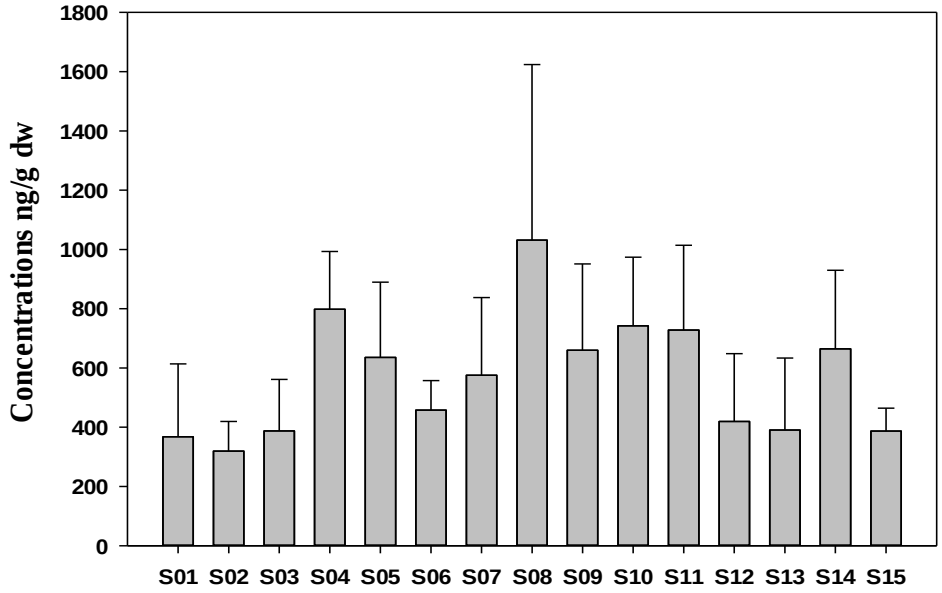


Figure 4-2: Total PAH concentration across the sampling sites

In the case of individual PAH concentration, a relatively large difference was observed between the lower molecular weight PAHs (LPAH) (11-129 ng/g) and the higher molecular weight PAHs (HPAH) (49-422 ng/g). HPAH such as Fluoranthene (417ng/g) and Pyrene (422 ng/g) were always present as the dominant PAHs across all sites showing similar compositional pattern. Similarly, in the case of the LPAH (PHE and ANT exempted), it was interesting to note the moderate concentration levels of naphthalene (NAP) across most of sampling sites (S-03 to S12). This pattern exhibited by NAP was subsequently attributed to the proximity of the sampling sites to sources of anthropogenic activities (marinas, boat ramps and ferry activities) that contribute to localized input of PAH from unburned fuel, that was either exhausted by a type of carburetted two-stroke powered engine or by direct oil spillage. The occurrence of NAP in the sediment samples was also consistent with previous PAH studies on the Brisbane River (Kayal. 1990), Georges River estuary in Sydney, Australia (Brown et al. 1992) and the Mersey Estuary, England (Vane et al. 2007).

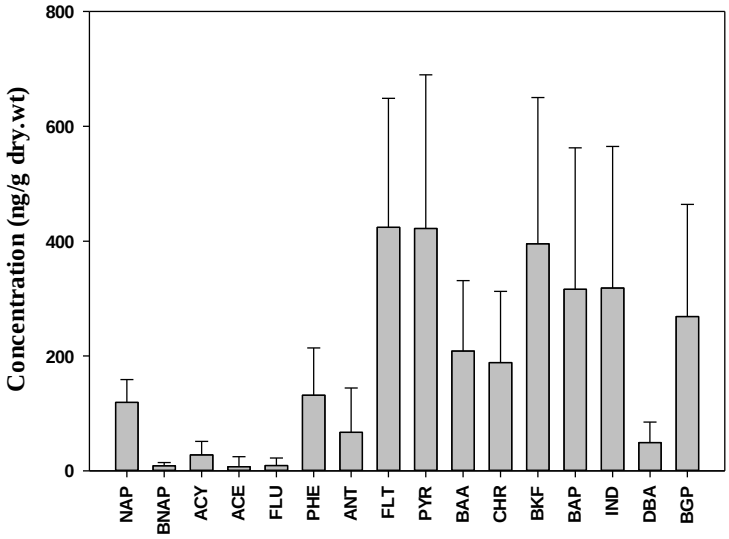


Figure 4-3: Mean PAH concentrations measured (ng/g)

4.4. COMPARISON OF PAH LEVELS WITH THOSE FROM OTHER AREAS

The total PAH concentrations (Σ16PAHs) have been widely used to evaluate anthropogenic pollution levels in the environment (Sun et al. 2012). Therefore, in order to understand the magnitude of PAH concentrations in the present study area, the reported PAH concentrations in sediment was compared with results from other urban water-sheds around the world as indicated in Table 4-1. The total PAH concentrations in the present study (1,038 ng/g) was similar to those detected from the Daliao (1,607 ng/g) (Men et al. 2009) and Yangtze (2,936 ng/g) (Wang et al. 2012) Rivers. However, the reported PAH concentrations were higher than concentration levels observed in sediments from the Gulf of Mexico (403 ng/g) (Wang et al. 2011), Leizhou Bay in South China (320 ng/g) (Huang et al. 2012), and lower in concentrations with reported PAH levels from the Mersey Estuary in the United Kingdom (3,766 ng/g) (Vane et al. 2007) and the Susquehanna River, USA (18,000 ng/g) (Ko et al. 2006).

Furthermore, the PAH concentrations were also found to be considerably lower than the concentration level from the previous study reported for the Brisbane River (11,650 ng/g) (Kayal. 1990) and the Georges River, Sydney, Australia (5,600 ng/g) (Brown et al. 1992). The reported results were also much lower when compared with highly polluted water-sheds such as the Sydney Harbour (380,000 ng /g) (McCready et al. 2000). Therefore, it could be concluded that the PAH concentrations in surface sediments from the selected sampling sites from the Brisbane River were at low to moderate concentration levels (i.e. ΣPAHs = 100 – 1000 ng/g), on the basis of PAH

pollutant level classification ; (a) low, 0-100 ng/g; (b) moderate, 100-1000 ng/g; (c) high, 1000-5000 ng/g; and (d) very high, > 5000 ng/g suggested by Baumard et al. (1998). The relatively low level of PAH contamination in sediment may be attributed to the stringent environment laws for water quality in the Brisbane River (DERM. 2010).

Table 4-1: Comparison of total PAH concentration in surface sediments with sediments from other urban water-sheds around the world.

Locations	N	Total PAHs (ng/g)	Mean (ng/g)	References
Yangtze estuary, China	16	77 - 2,936.	449.8	(Wang et al. 2012)
Gomti River, India	16	5 - 3,723	697	(Malik et al. 2011)
Huaihe River, China	16	85 - 935	480	(Feng et al. 2012)
Daliao River, China	16	276 - 1,607	743	(Men et al. 2009)
Susquehanna River, USA	16	70 - 18,000	-	(Ko et al. 2006)
Boston Harbor, USA	16	7,300 - 358,000	-	(Wang et al. 2001)
The Gulf of Mexico, North America	28	52 - 403	305	(Wang et al. 2011)
Vancouver Habour, Canada	15	99 – 11,000	-	(Bolton et al. 2003)
Santos Estuary, Sao Paulo, Brazil	17	4,000 - 7,550	-	(Martins et al. 2011)
Lenga Estuary, Chile	17	290 - 6,118	2025	(Pozo et al. 2011)
Brisbane River, Australia	16	3,940 - 16,110	-	(Kayal. 1990)
Sydney Harbour, Australia	17	<100 – 380 000	-	(McCready et al. 2000)
Spanish Northern continental shelf, Spain	16	22 - 47,528	-	(Viñas et al. 2010)
Mersey Estuary, U.K	16	626 - 3,766	-	(Vane et al. 2007)
Brisbane River, Australia	16	334 - 1,038	186	Present Study

N represents the number of PAHs that were investigated

4.5. PAH INTERRELATIONSHIPS

It is shown that where PAH compounds have a common source, there is more likely to be a correlation between their concentrations (Gilbert et al. 2006). Therefore, Pearson correlation coefficients were observed for PAH concentrations from all sampling sites during the entire study period have been presented in the supplementary material (Table A1-1). A statistically significant correlation ($P<0.01$) was consistently indicated for HPAH, suggesting a common source and particularly those from similar anthropogenic sources. Statistically significant correlation were mainly exhibited by structural isomers pair which include; FLT/PYR (0.88), BaA/CHR (0.91), and IND/BgP (0.83), respectively. Significant correlations were also observed between these PAHs with identical structure and other HPAH such as between BAP/BaA with correlation coefficient of 0.91, BaP/CHR (0.84), IND/BaA (0.94), IND/CHR (0.88), IND/BaP (0.96), BgP/BaA (0.83). The results reveal that the PAH compounds were possibly derived from a common source and were also widely distributed around the study area. In contrast, the LPAH showed weak correlation throughout the sampling sites. However, strong correlation was observed between NAP/ACY, NAP/FLU, PHE/ACE. The weak correlations between LPAH compared to the HPAH supports the evidence that they may also originate from different sources (mainly petrogenic and pyrogenic). The results of the analysis of correlations between individual PAH were confirmed by the application of the diagnostic ratio analysis that is explained in Section 4-8 of this thesis.

4.6. CHARACTERISATION OF SEDIMENT PHYSICAL AND CHEMICAL PROPERTIES

As discussed in the chapter two of this thesis, the fate of PAHs in the aquatic environment is strongly influenced by physicochemical properties such as organic carbon content and grain size distribution, which apparently play an important role in the partitioning of PAHs in the sediments. Results from the measurement of sediment physiochemical properties have been outlined in Table 4-2.

Sediment pH has been used to provide information regarding the nature of sediments under investigation. Therefore, it serves as an important variable controlling the bioavailability of organic contaminants (Simpson et al. 2005). The pH levels were based on the range in sediment pore water pH levels (7 - 8.5), while sediment pH levels evaluated ranged from 7.6 to 8.6. In this regards, there was no significant trend shown for the sediment pH among the sampling sites. In contrast, electrical conductivity (EC) values of the river were slightly variable and ranged from 165-320 μS /cm with a mean value of 303 ± 56 μS/cm. Moderate EC values were found at sites, S-01 (291 μS /cm) and S-07 (293 μS /cm), respectively. Site S-01 was located close to the river mouth and it is representative of the saline water from the river estuary. Therefore, the EC level could tentatively be attributed to the salt content in the sediment samples. However, there was no obvious explanation for the elevated EC observed at site S-07.

Table 4-2: Sediment physico-chemical characteristics obtained from the sampling sites

Sites	pH	Electrical Conductivity (µS)	Organic Matter Content (%)	Clay (%) <2.0µm	Silt (%) 2- 50 µm	Sand (%) 50-2000µm	Sediment Texture	TOC (%)
S-01	7.6	260	0.15	50	38	12	Clay	2.07
S-02	7.8	208	0.19	58	40	2	Silty Clay	1.60
S-03	8	193	0.22	48	42	10	Clay	1.37
S-04	7.9	275	0.20	87	11	2	Clay	1.49
S-05	8.2	289	0.14	45	35	20	Clay	2.27
S-06	8.2	272	0.18	46	42	12	Silty Clay	1.74
S-07	7.9	268	0.28	88	4	8	Clay	1.05
S-08	8.6	260	0.19	55	41	4	Silty Clay	1.60
S-09	7.9	328	0.16	60	32	2	Clay	1.91
S10	8.0	314.	0.31	40	52	8	Silty Clay	0.95
S11	8.2	313	0.58	72	20	8	Clay	0.43
S12	8.2	296	0.38	72	16	12	Clay	0.74
S13	7.9	305	0.20	64	24	12	Clay	1.55
S14	8.6	318	0.45	50	38	12	Clay	0.60
S15	7.9	248	0.42	32	62	6	Silty Clay	0.64

4.6.1. Sediment Geochemistry Based on Total Organic Carbon Content

Total organic carbon content (TOC) has an important influence on the distribution of PAHs in the aquatic environment as it also aids in the provision of binding sites for their adsorption in sediments (Simpson et al. 2005). The TOC obtained varied between the sampling sites ranging from 0.60 to 2.27%. However, moderate TOC levels were mostly found at the sampling sites (S-01 to S-09), located at the industrial area. Statistical analysis of correlation was carried out to investigate the relationship between the concentrations of PAH and sediment organic carbon content and to determine if this could be correlated with PAH distribution. No significant correlation was found between the organic carbon content and the total PAHs concentrations for all the sediment samples (r^2=0.0443, p=0.572) (Figure 4-4). This results was also consistent with a previous PAH study conducted for sediments from the Brisbane River (Kayal. 1990).

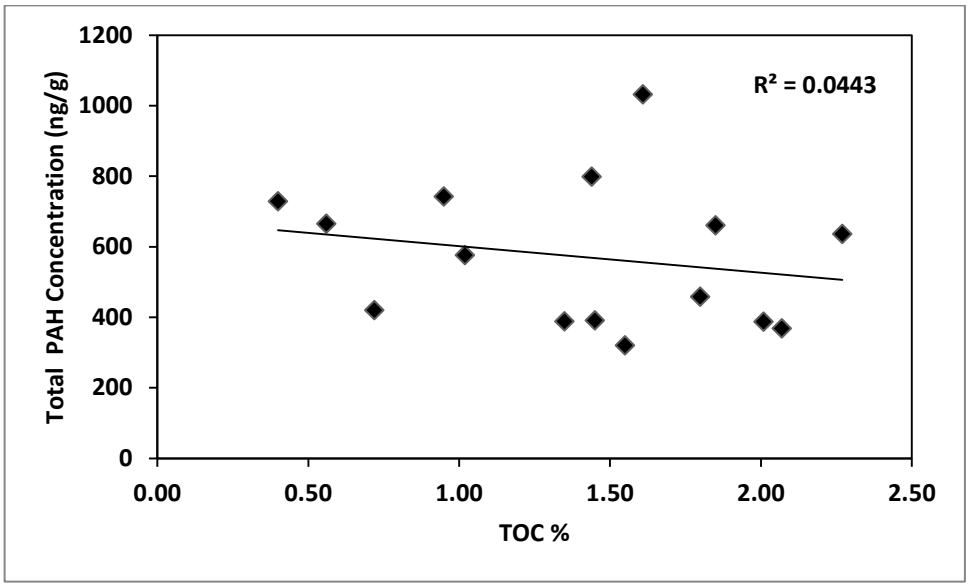


Figure 4-4: Correlation between the total PAH concentration and TOC

Therefore TOC was subsequently ruled out as a factor influencing PAHs distribution in sediment. A plausible explanation for the weak TOC correlation with the total PAH was the masking of sedimentary PAH by diffuse sources such as wood debris, black carbon (soot), ash and coal tar. It has also been suggested that sediments with high organic carbon contents generally contained high values of PAHs while the sediments with low organic carbon contents generally had low level of PAHs (Xu et al. 2007). The finding from the study (i.e. low to moderate PAH concentrations) suggested that a weak relationship exists between the sediment organic carbon content and PAH levels.

4.6.2. Sediment Geochemistry Based on Grain Size Distribution

The sediment characteristics showed that grain size distribution in most sites was predominantly composed of fine-grained components (clay/silt fraction; <2-50 µm), and to a lesser extent, coarse sediment component (sand fraction; 50-2000 µm). A possible explanation for the high proportion of the fine-grain sediment fraction could be attributed to the collection of sediment samples from areas of less intense water movement, marine sedimentations and other terrigenous input. The sediment texture across the sampling sites S-01 to S14 was predominantly silty-clay, while site S15 had a silty clay loam sediment texture type. As a result, sediments had high percentage clay and silt content (16-88 %) and a low percentage of the sand fraction (2-12 %), showing variable grain size distribution pattern between the sampling sites.

The sediment grain size distribution was further examined to explore the relationship between the major fractions (% Silt & % Clay) and the total PAH concentrations from the sampling sites. There was no correlation (r^2 = 0.020; P = 0.466) between the total PAH concentrations and silt/clay fractions (Figure 4-5), showing that the grain size distribution had a least influence on the distribution of PAHs in the sediments and shown as a minor factor affecting the adsorption of PAHs by sediments.

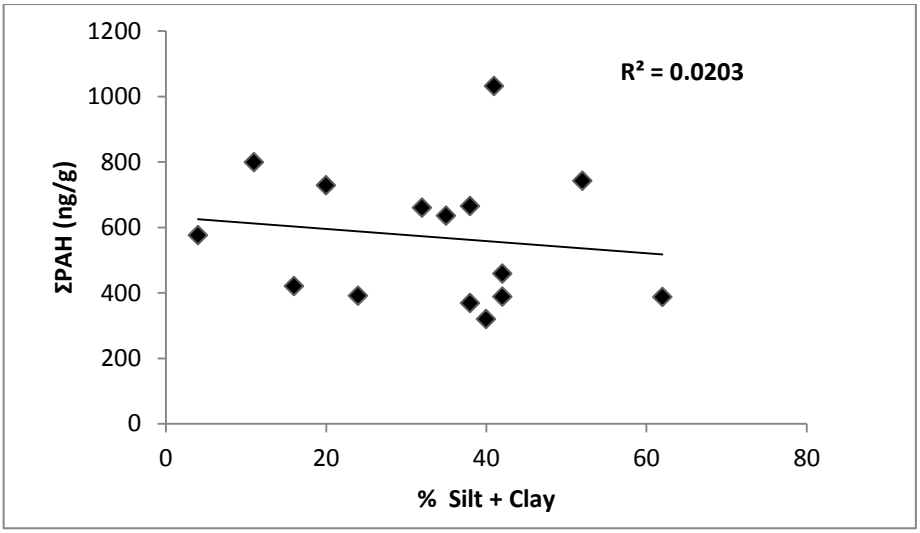


Figure 4-5: Correlation between the ΣPAH (ng/g) and % Silt+Clay in sediments

4.7. ASSESSMENT OF SEDIMENT TOXICITY

4.7.1. Effect and Threshold Range (Biological Approach)

The potential toxicological impacts of PAH in sediments were assessed by comparing PAH concentrations with the numerical effect-based sediment quality guideline values (SQGs). Since PAHs commonly occur as complex mixtures in environmental samples, substantial efforts have been undertaken to predict the toxicity of PAH mixtures rather than that of individual PAHs (Dupree et al. 2007).

As earlier described, the SQGs such as ERL and ERM values are useful for addressing sediment quality issues with regards to the protection of the aquatic environment. The ERL and ERM values were intended to define chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biological effects in the aquatic ecosystem (Xu et al. 2007).

The measured PAH mean concentrations were compared with the ERL and ERM values as shown in Table 4-3, indicating that PAH concentrations obtained during the study period were below the ERL and ERM values. As a result, PAH concentrations in the 15 sampling sites were in the minimal adverse effects range and therefore pose low ecological risk in the sediments. In addition, the total PAHs concentrations (1038 ng/g) from this study were far less than the ERL value (4022 ng/g). Thus, the probability of adverse effects caused by PAH would be low. Similarly, concentrations of total PAHs obtained were below the Effects Range-Median (ERM) value (44792 ng/g), suggesting that adverse effects on benthic organisms living in and coming into contact with the sediments were less likely occur.

Table 4-3: Standard pollution criteria of PAH components for sediment matrix (ng/g)

PAH	ERL	ERM	TEL	PEL	*Mean Concentration Present Study
NAP	160	2100	34.6	391	23.4
BNAP	NA	NA	NA	NA	2.1
ACY	16	500	6.71	88.9	6.8
ACE	44	640	5.87	128	4.5
FLU	19	540	21.2	144	5.2
PHE	240	1500	86.7	544	25.7
ANT	85.3	1100	46.9	245	15.1
FLT	600	5100	113	1494	83.5
PYR	665	2600	153	1398	84.3
BAA	261	1600	74.8	693	40.7
CHR	384	2800	108	846	36.8
B[b+k]F	NA	NA	NA	NA	78.4
BAP	430	1600	88.8	763	61.9
IND	NA	NA	NA	NA	62.2
DBA	63.4	260	6.22	135	9.8
BGP	NA	NA	NA	NA	52.7
Total PAH	4022.0	44792.0	1684.0	16770.0	593

ERL: effect range low; ERM: effect range medium; TEL: threshold effect level; PEL: probable effect level; ∗: Average PAH concentrations relative to sediment's effect and threshold Range; NA: Not available

Similarly, the effect-based approach involving the threshold effect level (TEL) and probable effect level (PEL) was estimated, and the mean PAH concentrations was greater than TEL threshold value (1684 ng/g), implying that the sediments may likely cause adverse effects to benthic organisms. In contrast, the PEL threshold

value (16,770 ng/g) (Table 4-3) was greater than the concentration value reported for the entire study area. In particular, the individual PAHs were below their corresponding PEL guideline values and were suggested to pose no negative effect to benthic organisms in sediments.

4.7.2. PAH Carcinogenic Potencies (Toxicity Equivalency Quotient Approach)

In order to determine the carcinogenic potency of PAHs in the sediments samples, their toxicity equivalency quotient (TEQ) relative to BaP was estimated. The TEQ of individual PAH was calculated based on the toxic equivalency factor (TEF) values proposed by Nisbet and LaGoy (1992) as shown in the supplementary material (Table A2-1)

As shown in Figure 4-6, with the exception of the substituted PAH (BNAP), TEQ concentrations for the PAH varied across the sampling sites, ranging from 42-185 ng/g and having a mean concentration of (90 ± 14 ng/g). The highest TEQ concentrations were observed at sites S-04 (175 ± 45 ng/g) and S-08 (185 ± 38 ng/g) located in the industrial section. These sites were particularly close to a run-off drain and cargo vessel loading dock respectively, indicating the great influence of petrogenic and combustion sources. The lowest TEQ concentration (42 ± 17 ng/g) was observed at site S15, located in the urban section of the river. The sum of the total carcinogenic potencies of the PAHs (ΣTEQ_{carc}) varied slightly between from 12-60 ng/g with an average concentration of 12 ± 9 ng/g. TEQ concentrations also varied across the sampling sites and were in agreement with the TEQ concentrations reported from a previous PAH study on the Brisbane River (Shaw et al. 2004), where

sites closer to the river mouth had lower TEQ concentrations due to dilution in PAH input as a result of severe flushing. In contrast, runoff from roads and street drains adjacent to the river could account for the increased TEQ concentration towards the urban areas.

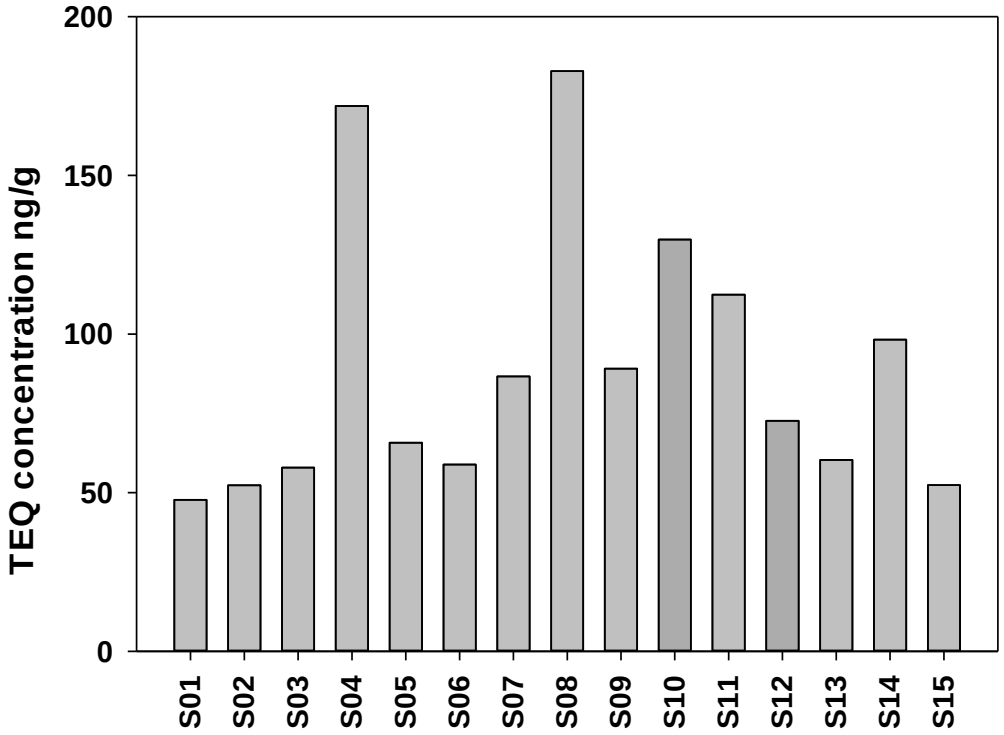


Figure 4-6: PAH TEQ concentrations observed for the sampling sites

As expected, the PAH_{TEQ} concentrations obtained for the 4-6ring PAH, particularly for carcinogenic PAHs was higher than the concentrations for the 2-3-ring PAH compounds. Regarding individual carcinogenic PAH, BaP (60 ng/g) and DBA (9.0 ng/g) had higher TEQ concentrations, and could indicate probable adverse effects to aquatic organisms. This observation tends to agree with a recent PAH assessment, where Guo et al (2011a), observed the high contribution of TEQ from BaP and DBA in lake sediments.

Generally, the PAH TEQ concentrations recorded from this study were lower than the TEQ values reported in surface sediments from other urban water-sheds, Lake Hongfeng (334 ng/g), Southwest China (Guo et al. 2011a), Fenhe watershed (590 ng/g), China (Tian et al. 2013) Meiliang Bay. In summary, the TEQ of the PAHs were highly variable in samples collected from the urban and industrial areas and except for few sites, the findings indicated that PAHs measured in the sediments would probably not cause any immediate toxic effect to aquatic species in the Brisbane River. ‘

4.8. PAH SOURCE IDENTIFICATION

4.8.1. Evaluation of the Diagnostic Ratio

The pyrogenic and petrogenic sources of PAHs can be assessed using the diagnostic PAHs ratios, including ANT/(ANT + PHE), FLU/(FLU + PYR), BaA/(BaA + CHR), and IND/(IND + BgP), to qualitatively distinguish anthropogenic PAHs inputs.

In this study, the diagnostic ratio obtained were obtained on cross-plots (Figure 4-7) with a range of 0.45-0.60, strongly indicating a pyrolytic PAH source. The ANT/(ANT+PHE) isomer pair ratio varied from 0.10-0.35, and showed that PAHs were primarily derived from combustion (ANT/(ANT + PHE) >0.10), with no occurrence of PAHs originating from petroleum. Similarly, the FLU/(FLU + PYR) isomer pair ratio (0.50-0.60) also showed that combustion was a potential source of PAH among the sampling sites. The congested clusters in the BaA/(BaA+Chr) vs FLU/(FLU + PYR) cross plot with ratio (0.44-0.62) could indicate that the PAH sources were mainly from combustion sources from all sampling sites. Similarly, a diagnostic mass ratio was obtained for the IND/(IND+BgP) vs FLU/(FLU + PYR)

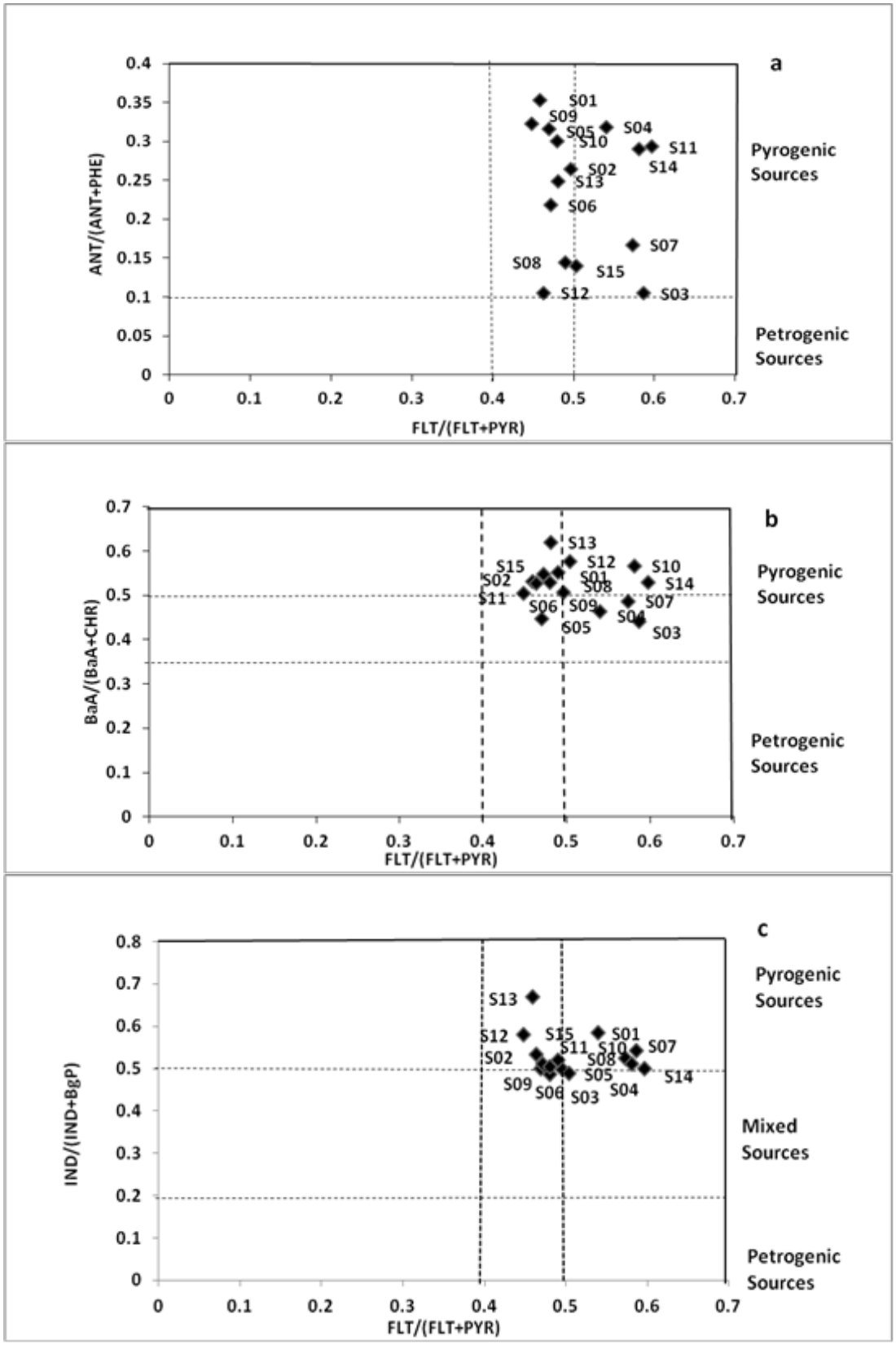


Figure 4-7: Cross plots for PAH diagnostic ratio analysis in sediments (a)Ant/(Ant + Phe);(b) BaA/(BaA+Chr); (c) Ind/(Ind+BgP).

cross plot and ranged between 0.49-0.67. The ratios were mostly higher than 0.5; this also indicated combustion sources as the PAH sources at the sampling sites. The data of the distribution patterns of the diagnostic PAHs ratios is highlighted in Table 4-4.

Table 4-4: Diagnostic ratios results obtained from the sampling sites

SITE ID	ANT/(ANT+PHE)	FLT/(FLT+PYR)	BaA/BaA+CHR)	IND/(IND+BgP)
S-01	0.14	0.49	0.55	0.52
S-02	0.26	0.50	0.51	0.50
S-03	0.10	0.59	0.44	0.54
S-04	0.32	0.54	0.46	0.59
S-05	0.32	0.47	0.45	0.50
S-06	0.22	0.47	0.55	0.51
S-07	0.17	0.57	0.49	0.52
S-08	0.35	0.46	0.53	0.67
S-09	0.32	0.45	0.51	0.58
S10	0.30	0.48	0.53	0.49
S11	0.29	0.58	0.57	0.51
S12	0.11	0.46	0.53	0.53
S13	0.25	0.48	0.62	0.50
S14	0.29	0.60	0.53	0.50
S15	0.14	0.50	0.58	0.49

In summary, the diagnostic ratios demonstrated that sediments from the 15 sampling sites contain a significant proportion of combustion-related PAH which might originate from a variety of sources (mainly fossil fuels). However, the diagnostic ratio indicators in the study could not give definite conclusions for PAH sources such as to account for PAH compounds that are indicative of petrogenic sources (petroleum). As a result, it could only provide qualitative information about the

contribution of PAH sources. In order to address the deficiency arising from its application in this study, hierarchical cluster analysis and principal component analysis were used to classify PAH into groups and to better identify their sources.

4.8.2. PAH Source Identification by Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) applied in this study, identified homogeneous groups of individual PAH with respect to the sampling sites. HCA rendered clusters which were projected on dendrograms on the basis of similarities between the PAH (Figure 4-8) and sampling sites (Figure 4-9). The output from HCA shows that sampling sites having similar PAHs contribution are clustered together. The PAHs were classified into four sub-groups, while sampling sites were discriminated into three sub-groups on the basis of common similarities. Therefore, species that clustered together in a group were assumed to come from a common source.

In considering clusters representing the PAHs (Figure 4-8), Group 1 consisted of the 2-3ring PAH (BNAP, FLU, ACE, ACY, ANT) and 5-ring PAH (DBA). Group 2 was characterised by the 3-4 ring PAHs (PHE, BaA, CHR) and act as tracers for diesel combustion (Larsen et al. 2003). Group 3 comprised of the 4-5ring PAHs (FLT, PYR, B[b+k]F) that are associated with pyrogenic sources such as the combustion of fossil fuel (gasoline, diesel and heavy fuel oils). Group 4 was comprised of BaP, IND, BgP, markers of petrol and diesel emission sources.

In Figure 4-9, different clusters of sampling sites are represented on a dendogram. These clusters are classified into three sub-groups Group 1 included sites S-01, S-02,

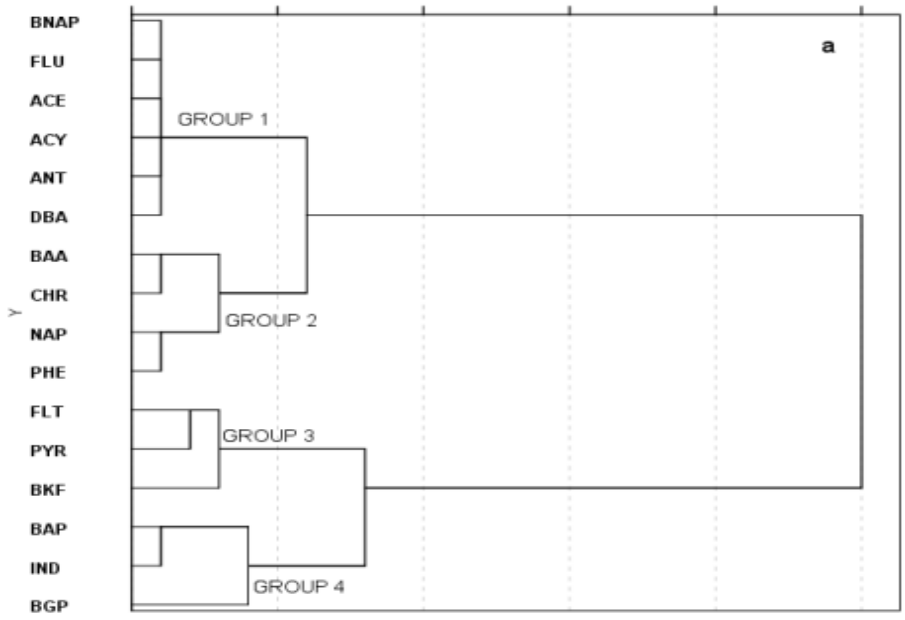


Figure 4-8: Dendrogram showing clusters between the PAHs

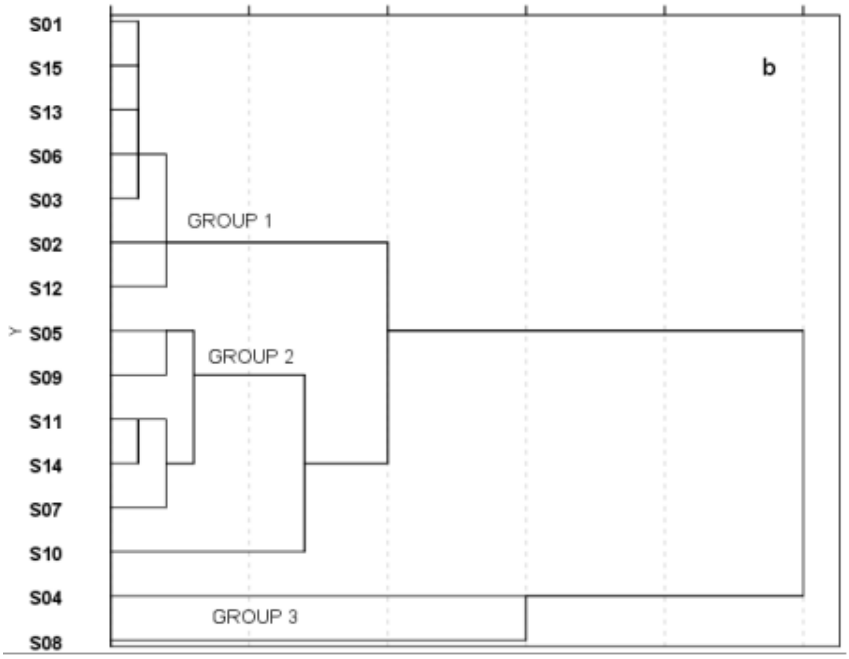


Figure 4-9: Dendrogram showing clusters between the sampling sites

S-03, located at the industrial section and close to the river mouth, while S-06, S13 and S15 were located in the urban section. These sites are regarded as the lowly

polluted sites. Group 2 included sites S-05, S-09, S-07, S10, S11, and S14 that were also located in the urban and industrial section, however, regarded as moderately polluted sites. Lastly, Group 3 only contained sites S-04 and S-08 were both located at the industrial section and therefore, regarded as the most polluted sampling sites.

4.8.3. Source Identification by Principal Component Analysis

Principal Component Analysis (PCA) of the individual PAHs and their relationship between the sampling sites was used to further investigate the potential sources of PAH contamination. In this study, the majority of the variance (71.11%) was retained by two principal components, with the first principal component (PC1) explaining 59.4%, while the second principal component (PC2) accounted for 11.7% of the total variance, respectively. As a result, the scores and loadings plot shown in Figures 4-10 & 4-11 were used to derive the relationship between the sampling sites and their associated PAHs, respectively.

The scores plot shows the grouping of three clusters A, B, C that represented different sampling sites located at the urban and industrial sections of the Brisbane River. Cluster A was generally made up of sites S-01, S-02, S-03, S-06, S12, S13, and S15. Cluster B comprised of sites S-04 and S10 while Cluster C was characterised by sampling sites S-05, S-07, S-08, S-09, S10, and S11. The loadings plot shows all the higher molecular weight PAH were found on the positive coordinate side of the PC1 axis while the lower molecular weight PAH were located on the positive-coordinate side of both PC1 and PC2 axes. PC1 had strong contributions from the higher molecular weight PAH (4-6 ring PAH), including the 3-ring lower molecular weight PAH (PHE and ANT). In contrast, PC2 had

significant positive loading for the lower molecular weight PAHs (2-3 ring PAH), except for BNAP. In relation to the objects in the scores plot, the less contaminated sites generally have positive loadings for PC2, whereas the highly contaminated sites were observed to have positive PC1 and negative PC2 loadings.

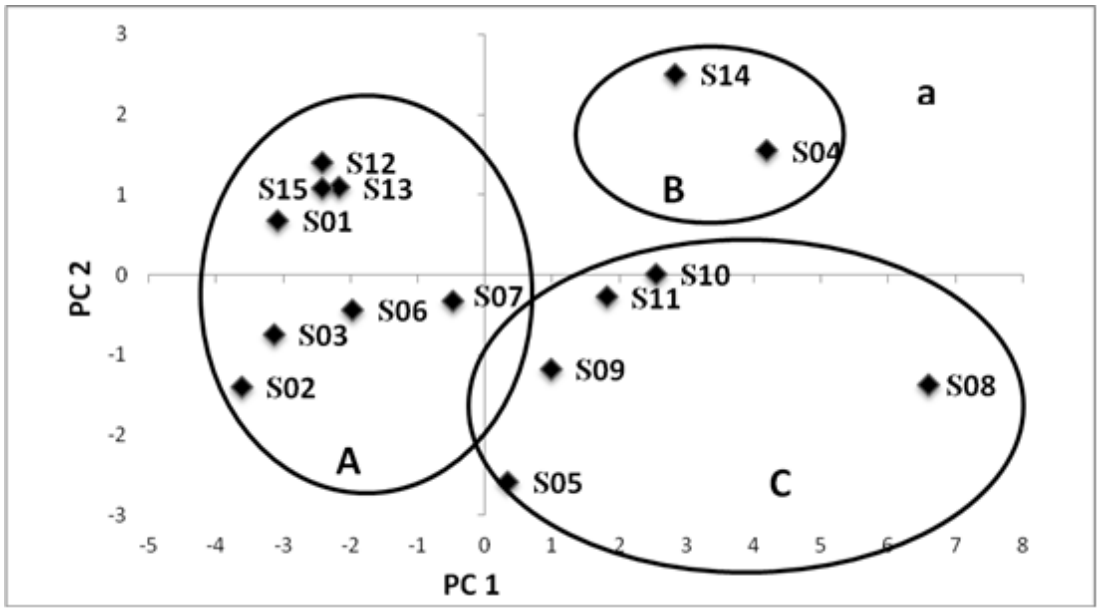


Figure 4-10: PCA Scores Plot for the first two principal components

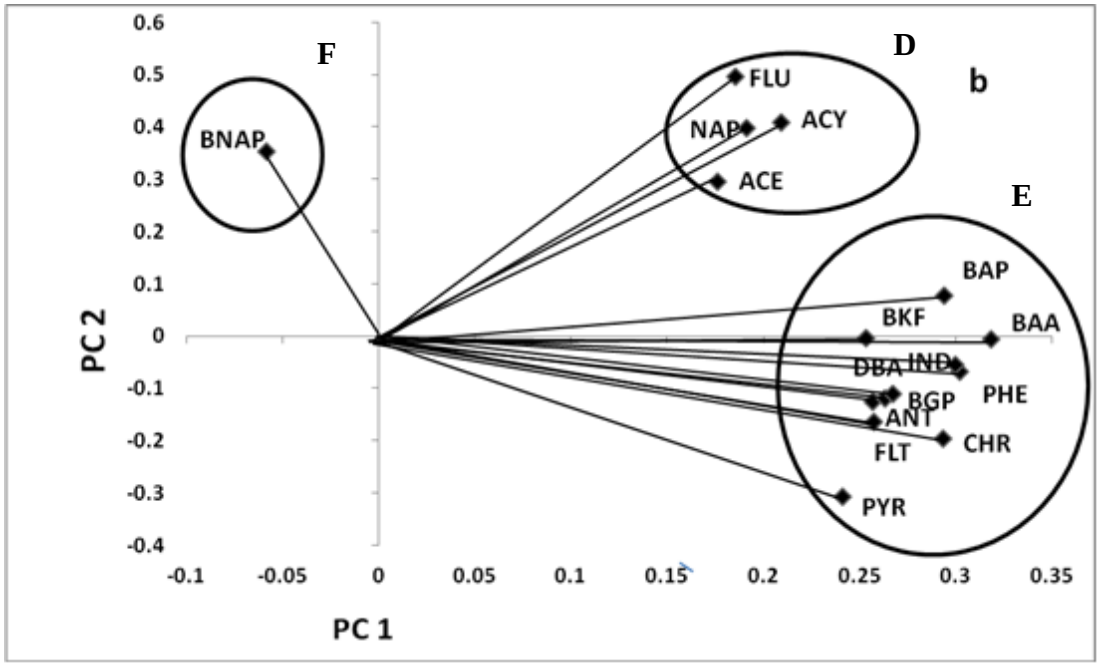


Figure 4-11: PCA Loadings Plot for the first two principal components

The loadings plot shown was subsequently used to ascertain the relationship among the variables in relation to the objects in the scores plot. The variables on the loadings plot were divided into three clusters D, E and F that were comprised of the 2- to 3- ring PAH and 4- to 6- ring PAH compounds and observed to be equidistant from each other. The 2- to 3- ring PAH (LPAH) in cluster D were strongly correlated with each other, therefore they were concluded to come from similar sources, mainly from petrogenic PAH sources. Similarly, the 4-6 ring PAH in cluster E also showed strong correlation between each variable and were characteristic of PAH from pyrogenic sources. Cluster F consists only of BNAP and was assumed to contribute little to the observed PAH trend in the sediments.

Based on the loadings of the HPAH in cluster E, it appears that they are associated with the sampling sites in cluster C, which are shown to be the most contaminated sites. Similarly, cluster D was comprised of loadings of the LPAH which were associated with the sampling sites in cluster B, which appeared to be less contaminated than sampling sites in cluster D and more contaminated than sampling sites in cluster A, which accounted for the least contaminated sampling sites. In order to further determine the relationship between the sites and their PAH inputs, the scores and loadings plots were examined more closely. The sites in cluster A showed no correlation with the variables from cluster E. However, they were shown to be orthogonal to variables in cluster D and therefore correlated with each other. Cluster E was characterised by the 4-6 ring PAH which are notable markers for coal, diesel and heavy oil combustion (Simcik et al. 1999; Larsen et al. 2003; Jiang et al. 2009). The observation was in agreement with potential anthropogenic sources that

were characteristic of the samplings sites. These include: heavy maritime and vehicular traffic.

In comparison with other PAH identification methods, PCA results were consistent with results from the HCA which showed similar patterns for the grouping of PAHs and the sampling sites. This confirmed the notion that the variables in the clusters may share similar PAH signatures and behave in a characteristic manner.

4.9. MCDM ANALYSIS

4.9.1. PROMETHEE Analysis

The PROMETHEE II method provided a complete outranking flow from the least to the most preferred location from the data matrix. The variables from the data-set were minimised (i.e. lower concentration levels preferred) in keeping with the assumption that sampling sites close to the river mouth will be the least contaminated by PAHs.

PROMETHEE net outranking flow values in Table 4-5, described the best results as sites with the lowest concentration of PAHs such as S-02, while the worst results were sites with the highest concentration of PAHs (S-08). In general, the sampling sites were classified into two groups indicating sites S-01, S02, S-03, S-05, S-06, S-07, S-12, S13 and S15 as the least polluted sites while sites S-04, S-08, S-09, S10, S11 and S14, were shown to be the most polluted sites. It is noteworthy that the PROMETHEE results were consistent with the results obtained from the HCA (Figure 4-8) and PCA scores plot (Figure 4-10).

4.9.2. GAIA Analysis

GAIA analysis provided similar principal components as described by the PCA analysis. The GAIA planes visually portrayed the relationship between the sampling sites and PAH concentration levels as well as the decision axis "π" (i.e. direction in which the most preferred sites are positioned). The GAIA plane shown in (Figure 4-12) accounted for most of the total variance (89.88%), thereby suggesting that only 10.12% of data variance was lost during the projection.

The results from the GAIA plane were clearly separated into two representative clusters (Figure 4-12). Cluster G comprised of the sites that were correlated with each other and have similar characteristics. They have been regarded as the most polluted sites in this study as they are oriented away from the decision axis (π).

Site (S-08) is shown to be the most contaminated site as it was the farthest from the decision axis (π).The GAIA plane complemented observations obtained from the PCA analysis. Cluster G showed similar site number and characteristics when compared to the sites associated with Group 1 from HCA. In contrast, Cluster H consisted of sites that had their vectors oriented towards the decision axis (π) and as a result, classified as the least polluted sites in the study area. In a similar way, the sampling sites observed in Cluster H showed similar trends when compared with sites associated with Groups two and three, obtained from the HCA.

Table 4-5: PROMETHEE ranking of sampling sites showing the level of contamination from the best to the worst sites.

Rank	Sites	Net outranking flow (Φ)
1	S-02	0.24
2	S-03	0.20
3	S-01	0.15
4	S13	0.14
5	S15	0.12
6	S12	0.12
7	S-06	0.12
8	S-07	0.04
9	S-05	0.03
10	S-09	-0.08
11	S11	-0.12
12	S10	-0.14
13	S14	-0.20
14	S-04	-0.26
15	S-08	-0.36

Φ: represents the net performance flow used in the ranking of sites

Cluster I which had a long vector for PAH species such as BaP and IND, which were found to be strongly correlated with one another and relatively correlated with chemical species in Cluster K containing BGP, BaA, CHR, PHE, thereby showing similarities in the sources of each of the compounds. IND, BaA and CHR are regarded as tracers for diesel combustion engines; PHE has been attributed to diesel combustion, while BGP and BaP are known tracers for automobile emissions. BaP has been linked as a tracer of diesel combustion (Pies et al. 2008). The vectors of these chemical species were oriented in the opposite direction to the sites in Cluster G, suggesting a relationship between them.

Cluster L comprised of higher molecular weight PAHs (FLT, PYR, B[b+k]F) which were regarded as being similar in composition as their vectors were oriented in the same direction. They are also widely indicative of PAH combustion sources of diesel fuel emissions and oriented in the opposite direction of Cluster A. In general, Clusters L were characterised by heavy molecular weight PAHs and oriented in opposite direction to Cluster G. However, higher PAH concentrations where imbedded in the sites from Cluster G than for sites contained in Cluster H.

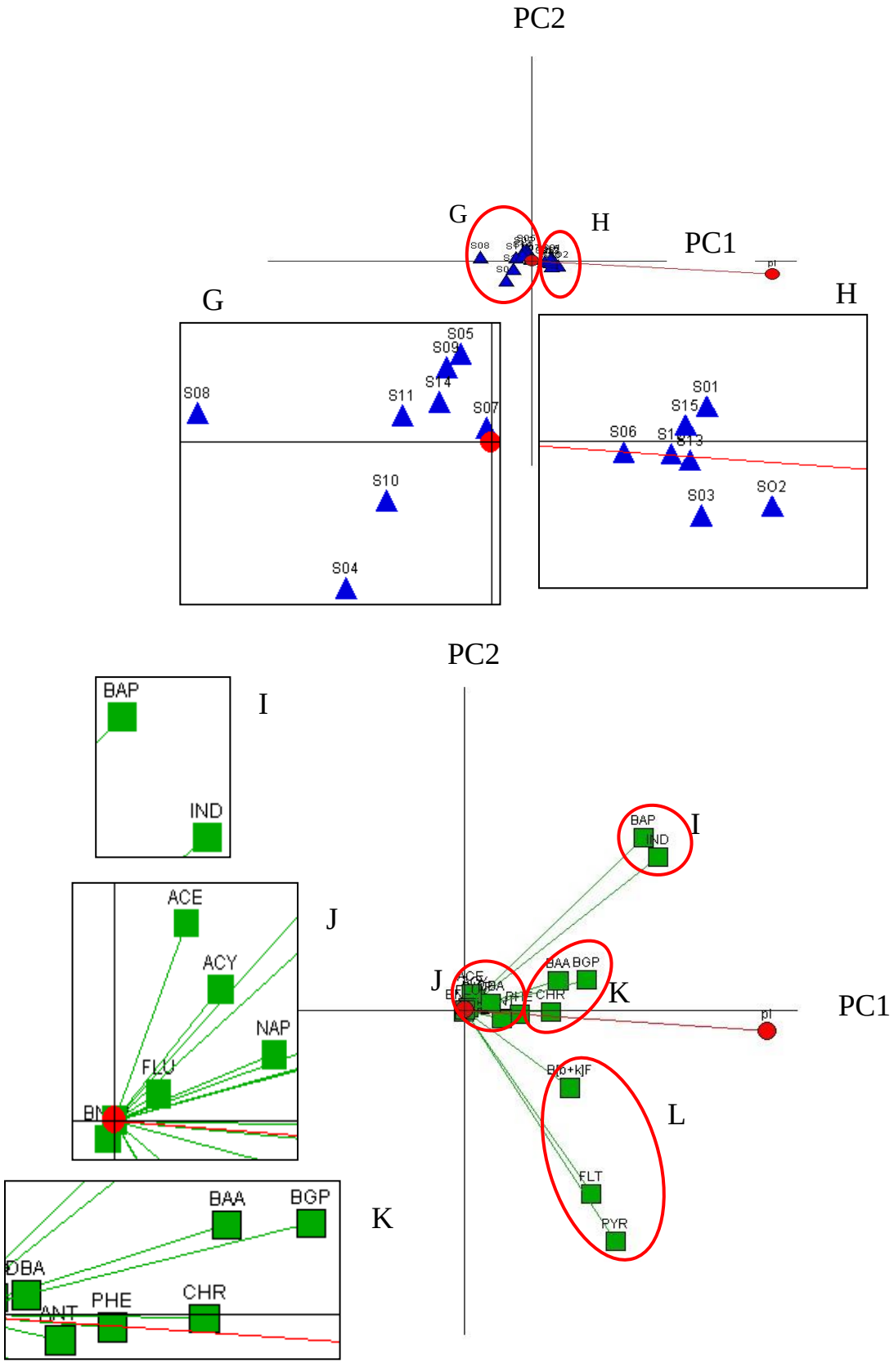


Figure 4-12: GAIA plane showing the separation of the sampling stations and PAH Clusters where Pi (π): indicate the decision axis; Boxes indicate amplification of PAH clusters

In summary, the sampling sites were ranked according to their degree of PAH contamination using both the PROMETHEE and GAIA methods. Results obtained from the ranking model provided net ranking information necessary to select individual sampling sites on the basis of its sediment quality. Although, MCDM provided ranking interpretation for the levels of PAH contamination across the study area; it was somewhat limited as it was unable to provide quantitative information in relation to the contribution of the sources of PAHs.

4.10. PAH SOURCE APPORTIONMENT

The receptor models were applied to estimate sources contribution of PAHs in the study. The PCA-APCS and PMF models extracted an optimum number of four factors for the identification of source profiles indicated in Figures 4-18 and 4-25. The identification of the number of factors was based on the distribution of PAH molecular markers (PAH source profiles). A squared correlation coefficient (R^2) of 0.9958 (Figure 4-13) and 0.9978 (Figure 4-14) was obtained for a linear relationship between the predicted and observed concentrations obtained for both models, respectively.

4.10.1. Source Apportionment by PCA-APCS

Factor 1 was mainly dominated by the higher molecular weight PAH (4-5 rings) which includes FLT, PYR and B[b+k]F and accounts for 55% of the sum of measured PAHs. The PAHs found are typical markers for fossil fuel emission, particularly from diesel exhaust emissions (Kavouras et al. 2001; Larsen et al. 2003).

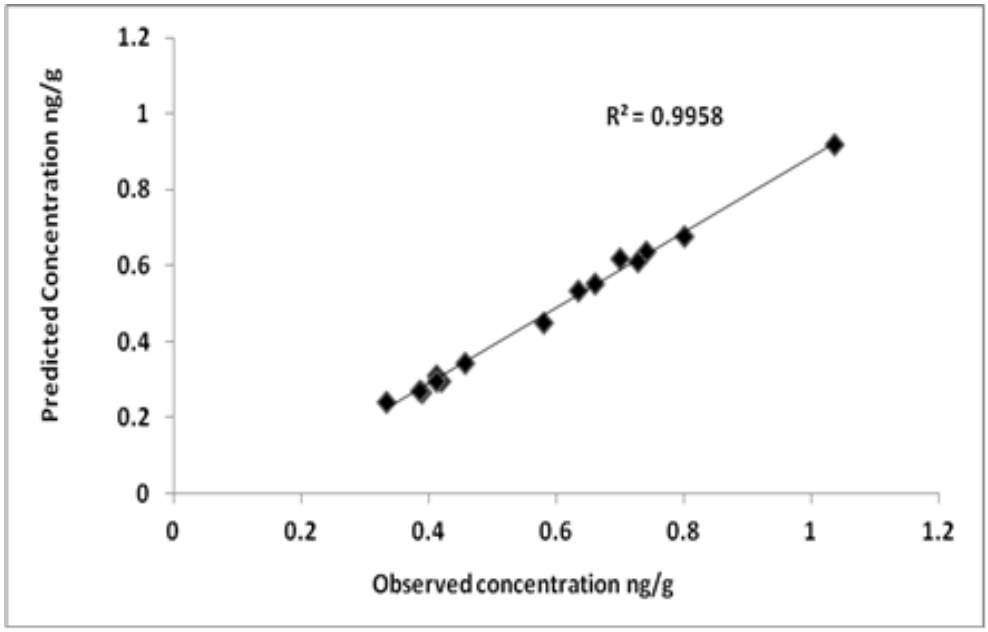


Figure 4-13: Observed versus Predicted PAHs concentrations in sediment samples (PCA-APCS Analysis)

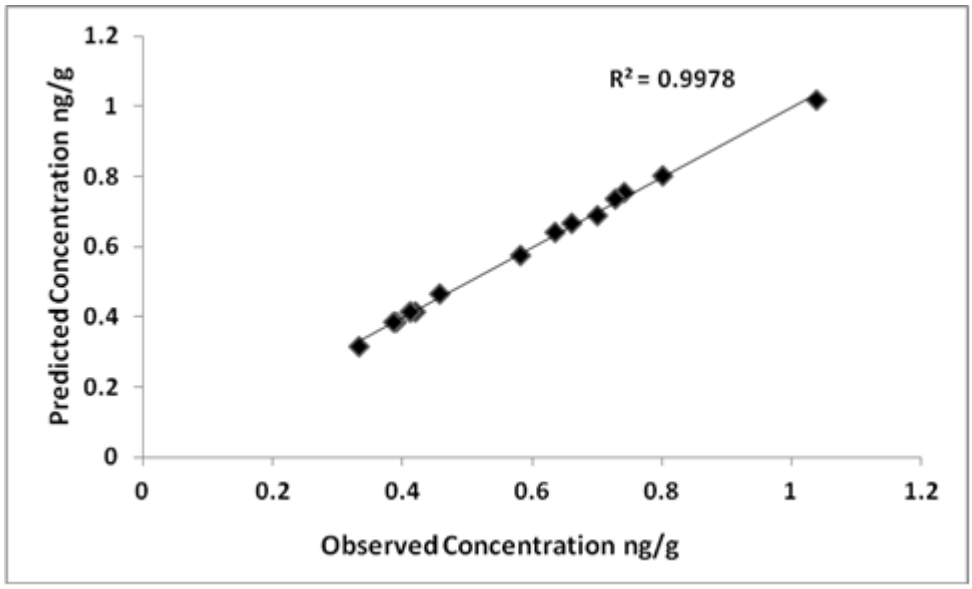


Figure 4-14: Observed versus Predicted PAHs concentrations in sediment samples (PMF Analysis)

The isomeric pair of FLT and PYR has also been identified as typical tracers for coal combustion and biomass burning (Sofowote et al. 2008; Liu et al. 2009b; Yang et al. 2013). However, coal is not a fuel source used in Brisbane, and therefore is seen as an unlikely PAH source.

Factor 1 was also moderately weighted with BaA, CHR and PHE, which are common markers for diesel emissions (khalili et al. 1995). Diesel emissions were linked to heavy anthropogenic activities around sampling sites S-05, S-08 and S-09. These sites were located close to a boat building and maintenance complex, a shipping dock and a fuel pier, commonly used for heavy industrial and maritime activities. These include the movement of large harbour-crafts such as cargo vessels, holiday cruise liners and tugboats around sampling sites. The PAH profile associated with the sampling sites was in good agreement with trends in the source contribution (Figure 4-15).

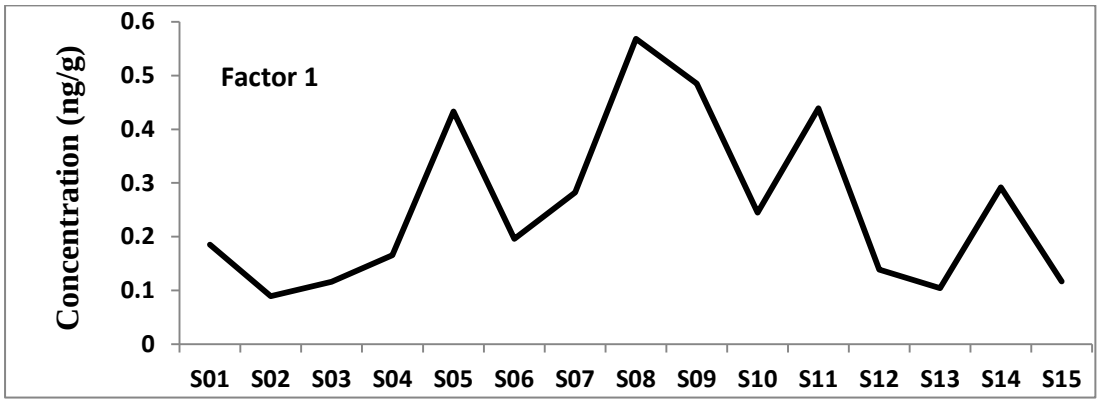


Figure 4-15: Source contribution derived for factor 1 from the PCA-APCS model

The source profile was also found to be consistent with the results obtained by other methods used for qualitative analysis of PAH in this study. When compared to the diagnostic ratio results, the values for the FLT/ (FLT+PYR) ratio ranged between

0.45-0.59 indicating a pyrogenic PAH source (combustion-related), that may to diesel exhaust emissions. The dominant PAHs provided by this factor were consistent with PAH profile results clustered in Group 3 from the hierarchical clustering analysis (HCA) that includes, FLT, PYR and B[b+k]F (Figure 4-8); and are characteristic of exhaust emissions. Hence, the PAH source from this factor was apportioned to diesel emission sources.

Factor 2 was represented by 16 % of the source contribution and was dominated by 2-3 ring PAH which include: NAP and ACY, which are indicative of petroleum oil spillage or uncontrolled leakage of vehicle oil and other possible petrogenic sources such as asphalt, brake and tyre wear from road surfaces (Latimer et al. 1990; Abrajano et al. 2004). In addition, the source profile was found to be heavily weighted with 5-6-ring PAH, notably DBA and BgP, which are shown as markers for emissions, particularly from petrol powered motor engines (Fraser et al. 1997). The sampling sites associated with this factor include: S-07, S-08, S10, S11, and S14, and was also well correlated with the source contribution assignment indicated in (Figure 4-16). Notably, sites S-07 and S11 were located close to two major bridges (Gateway and Story Bridges) that facilitate the regular movement of vehicular traffic within the metropolitan Brisbane area.

Sites S-08 and S10 were located close to a marina, shipping terminal and a ferry pontoon, while site S14 was located close to stormwater outlet near a public parking lot. PAH source profiles obtained from these sites were suggestive of petrogenic PAH sources which include: lubrication and crankcase oil from vehicles and light marine craft such as fishing and other pleasure boats. The source profile obtained for

this factor was in agreement with the PAHs clustered in group 1 from the HCA (Figure 4-8). The group showed a similar PAH profile which comprised mainly of ACY, ACE and FLU. In other words, factor 2 was subsequently attributed to mixed petroleum sources, consistent with mixed sources of petroleum and combustion-related emissions.

Factor 3 accounted for only 2% of PAH source contribution and therefore shown as a minor contributor in the PAH emission estimates. The PAH profile associated with this factor was mainly represented by the LPAH (i.e. ACE, FLU, PHE, and ANT).

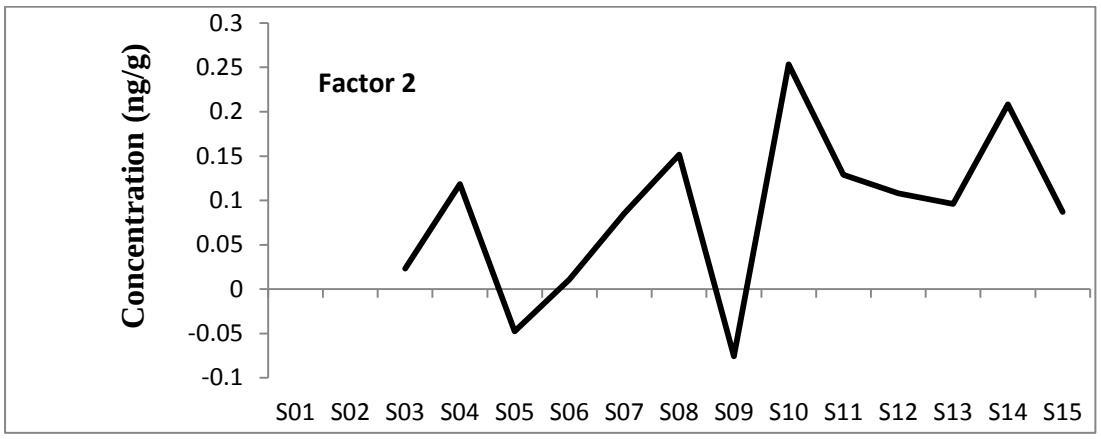


Figure 4-16: Source contribution derived for factor 2 from the PCA-APCS model

ACE and FLU have been noted as markers of petroleum-product residues (Medeiros et al. 2004), while PHE and ANT are regarded as indicators for lubrication oil and engine exhaust emissions, particularly from diesel-powered engines (Tavares et al. 2004). The PAH profile obtained from this factor dominated sediment samples collected from site S-04 and contained a distinct peak as shown in Figure 4-18. This may have been a function of the proximity of this site to a stormwater drain from the adjacent industrial complex. The factor was also moderately weighted by BaP, which is an indicator for petrol emissions (Simcik et al. 1999; Larsen et al. 2003). Therefore, factor 3 was attributed to an urban runoff source.

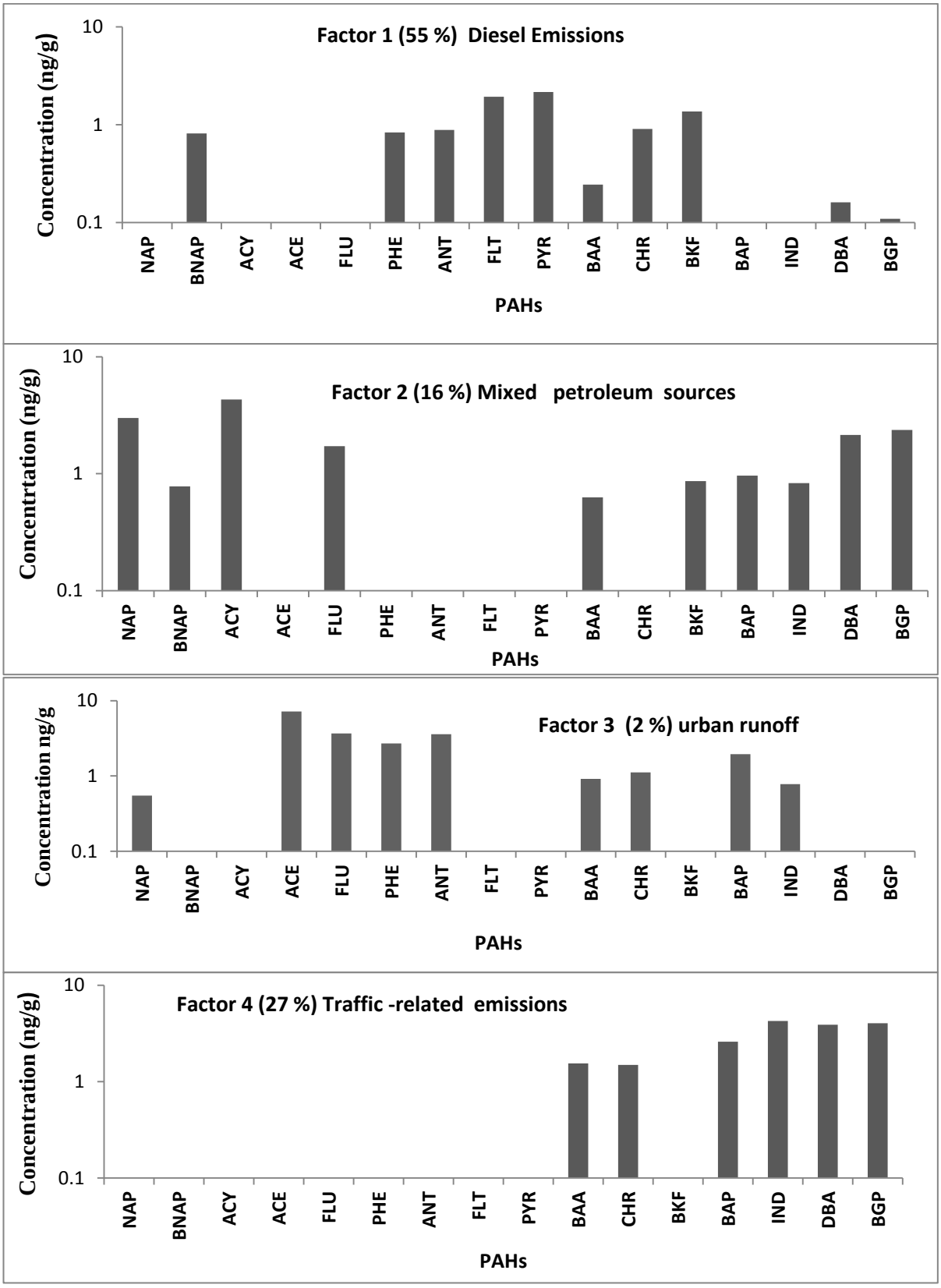


Figure 4-17: PAH source profile obtained for the PCA-APCS model

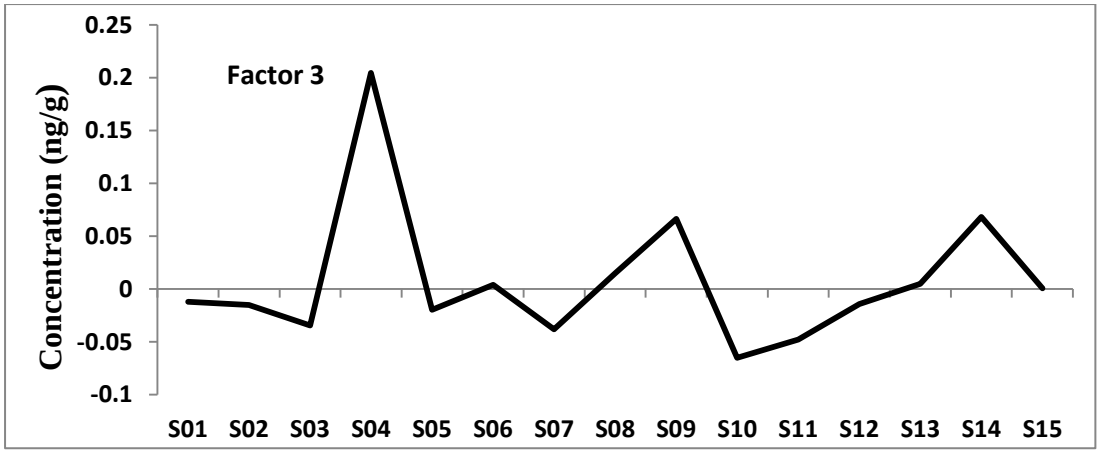


Figure 4-18: Source contribution derived for factor 3 from the PCA-APCS model

Factor 4 represented 27% of the source contribution and was comprised of high loadings of the 5-6 ring PAH which include: BaP, IND, DBA and BgP. IND and BgP have been regarded as the major tracers in diesel and gasoline engine emissions (Simcik et al. 1999; Larsen et al. 2003; Liu et al. 2009b). This factor was subsequently attributed to traffic-related petroleum discharges that are comprised of emissions from land and marine traffic. Emissions from land traffic were suggested to originate from vehicle exhaust emissions because the sampling sites were in proximity to the adjacent road networks, while emissions from marine traffic were suggested to arise from the intensive shipping activities that are carried out on the river. In comparison with other PAH source identification methods, the PAH profile obtained from this factor which included IND and BgP agreed with the diagnostic ratio results IND/(IND+BgP) that ranged from 0.49-0.67, indicating a characteristic combustion source for PAHs. The PAH profile obtained also in good agreement with the PAH profile which were grouped together in Group 4 from the clustering analysis and as a result shared similar characteristics.

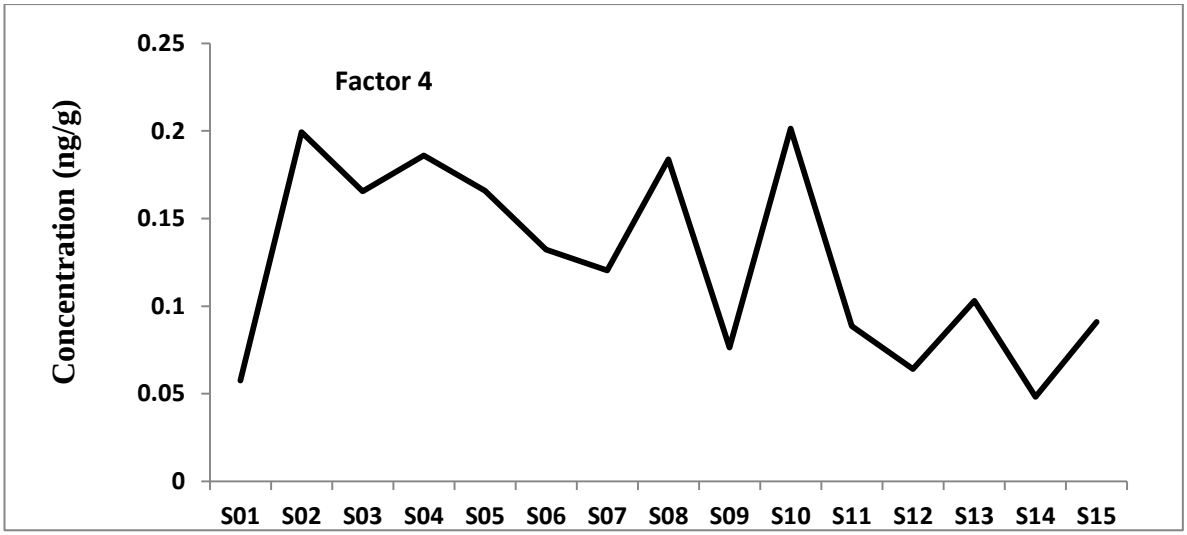


Figure 4-19: Source contribution derived for factor 4 from the PCA-APCS model

4.10.2. Source Apportionment by PMF

The identification of PAH sources by PMF was based on the source profiles shown in Figure 4-24. The first factor was represented by high contributions from HPAH, notably FLT, PYR and B[b+k]F which are tracers for diesel exhaust emissions (Kavouras et al. 2001; Larsen et al. 2003). This source profile was dominant in sampling sites S-05 S-08, S-09 and S11 and subsequently accounted for 41% of the PAH source contribution (Figure 4-20). Sampling sites S-05 S-08, S-09 were particularly close to areas associated with high industrial and maritime activities which comprised of marina, shipping yards and terminals. However, site S11 was situated around the area associated with marine activities mainly from the ferry services. It is worthy to note that diesel fuel has been reported to be responsible for about 80% of PAH emissions in Australia (Lim et al. 2005; Mostert. 2008). Therefore, this factor was attributed to a diesel emission source.

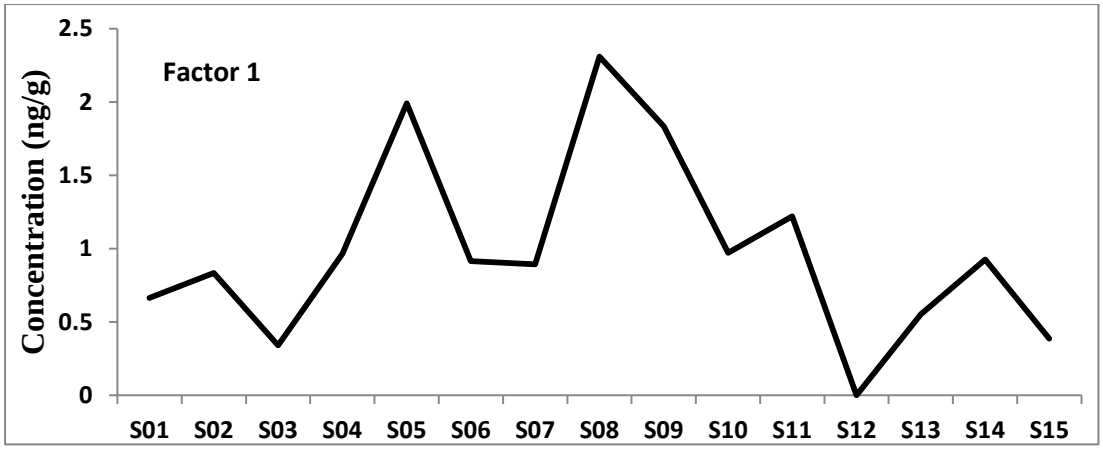


Figure 4-20: Source contribution derived from Factor 1 from the PMF model

Factor 2 was mainly dominated by 5-6ring PAH which include: BaP, IND, BgP and accounted for 22% of PAH source contribution. The PAH source profile were seen as traffic emissions tracers, particularly from petrol-powered motor engines (Simcik et al. 1999; Kulkarni et al. 2000). The PAH profile obtained was shown to be associated with urban activities close to sites S-03, S-07, S10, S12 and S14. As earlier described in the corresponding factor obtained from the PCA-APCS model; site S-07 and S11 were located close to the city's main bridges, S14 was located close to a stormwater drainage point, while S10 to S15 were close to marine transport facilities which include: a public boat ramp, marina and ferry services pontoon. Sampling site S-03 was located close to the refinery's loading dock and an area used for fishing. In other words, the significant contributions to the PAH profile was linked to petrol emissions from the motor-outboard engine and possible petroleum product spillage emanating from activities around the refinery's loading dock. Factor 2 was subsequently attributed to petrol emissions sources.

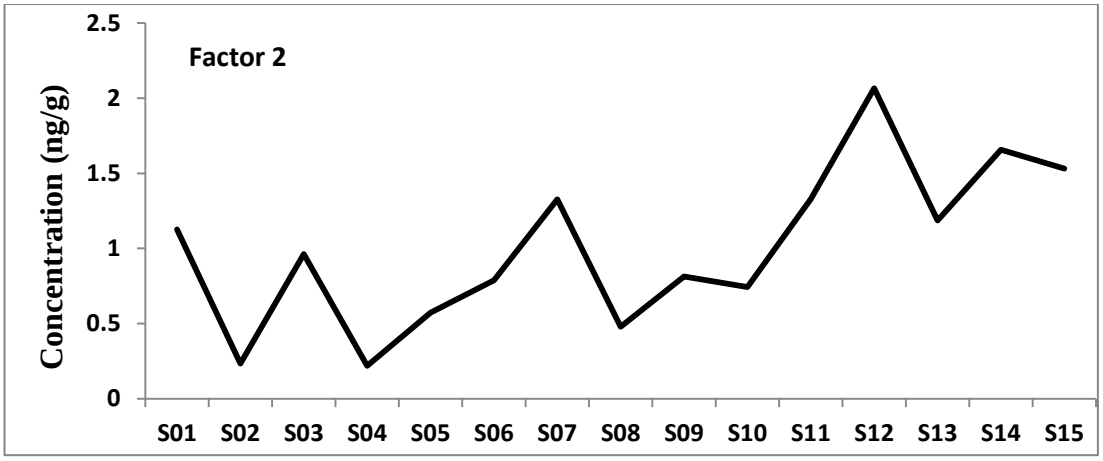


Figure 4-21: Source contribution derived from Factor 2 from the PMF model

Factor 3 accounted for 9% contribution from the model solution. The source profile obtained was highly weighted with BaP and IND, and has been identified as tracers for diesel and petrol engine emission (Sofowote et al. 2008; Liu et al. 2009b). The observation from the source contribution trend showed that the PAH profile obtained from this factor was highly dominating in site S-04, shown by the distinct peak in (Figure 4-22) and to a lesser extent S-08, S-09 and S14. Sites S-04 and S14 were close to urban runoff drains found in the industrial and urban areas. Therefore, the observed PAH profile was attributed to be an urban runoff PAH source.

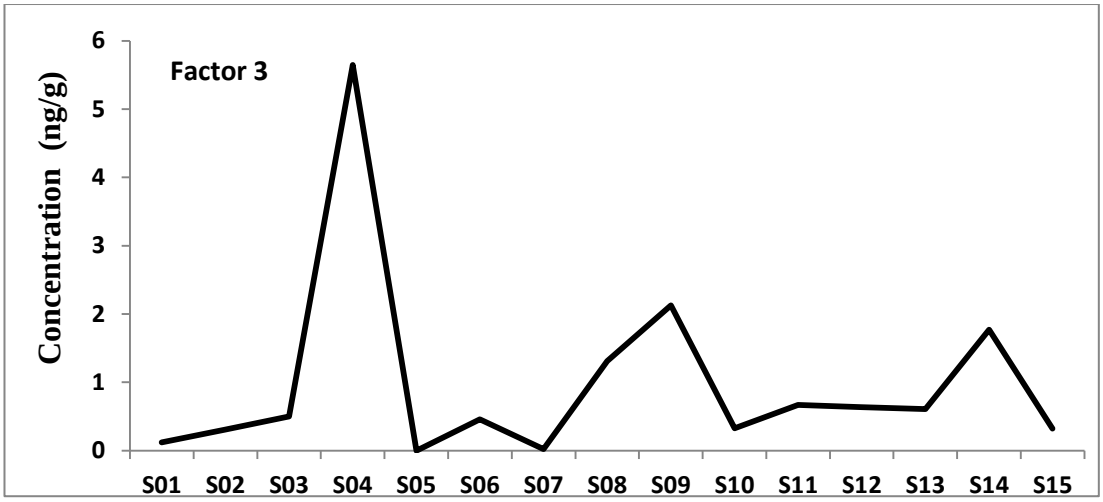


Figure 4-22: Source contribution derived from Factor 3 from the PMF model

The fourth factor accounted for 26% of the source contribution and was mainly characterised by high loadings from FLT, PYR and B[b+k]F. However, the benzofluoranthenes (B[b+k]F) are markers for diesel emissions (Zhang et al. 2011), while moderate loadings were shown for other PAH profiles, characteristic of traffic emissions (i.e. petrol and diesel emission). The observed PAH profile dominated the sediment samples collected in the industrial area which was clearly associated with intensive anthropogenic activities such as boat building and maintenance operations at sites S-04, S-06, S-07 and marine traffic (mainly emissions from commercial marine vessels such as passenger ferries) across sites S-08, S-09, S10 and S11 (Figure 4-23). Therefore, it was justifiable to attribute this factor to traffic-related emissions (notably, from marine diesel engines).

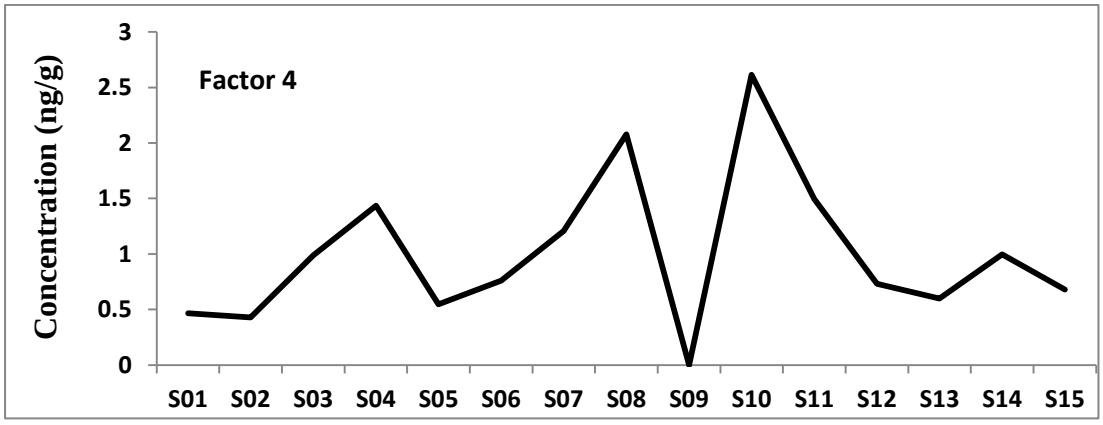


Figure 4-23: Source contribution derived from Factor 4 from the PMF model

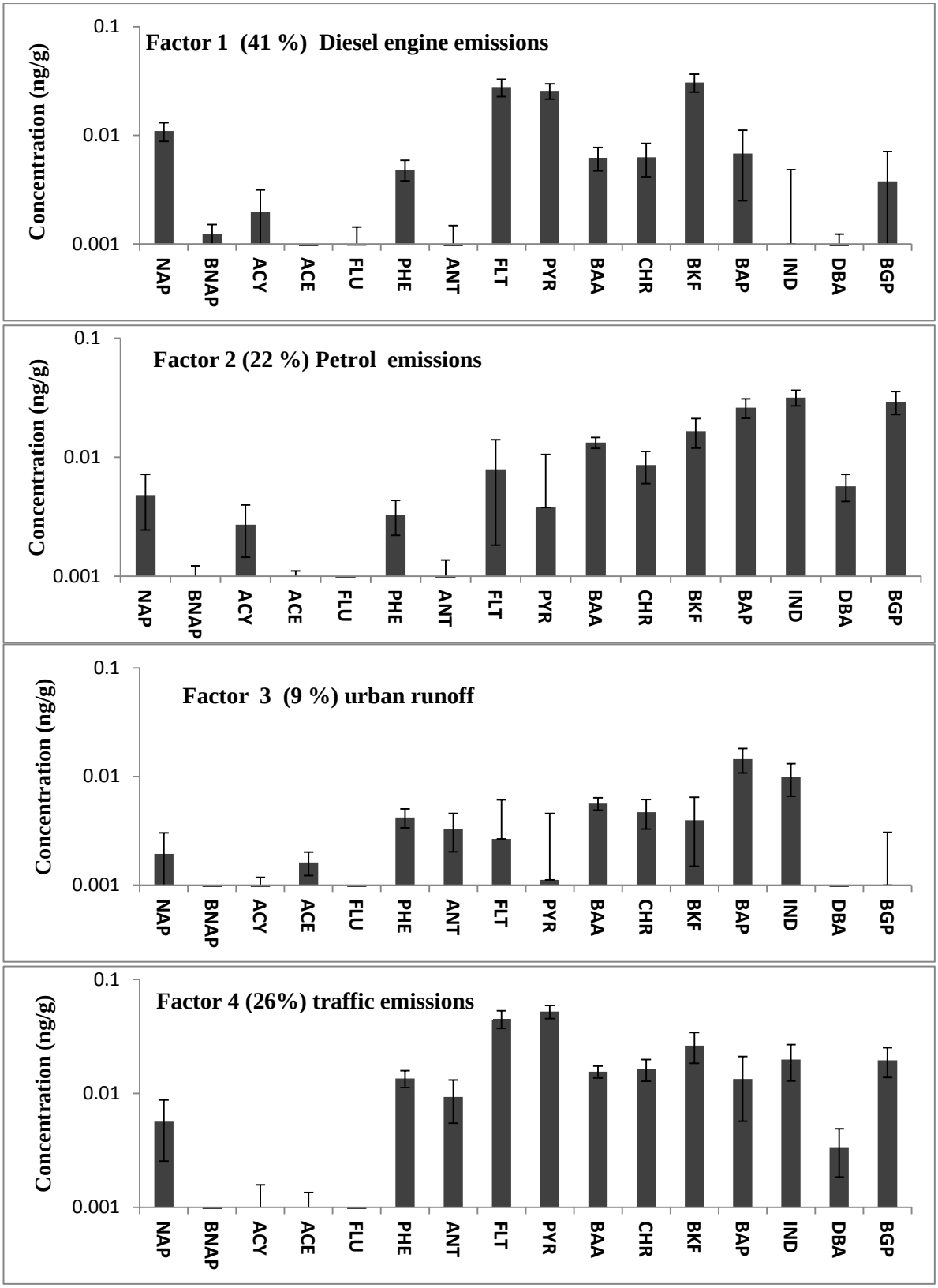


Figure 4-24: PAH source profile obtained for the PMF model [error bars show standard deviation (±1 s.d.)].

4.10.3. Comparison of PCA-APCS and PMF Results.

The application of receptor models for PAH source apportionment in sediments necessitated the comparisons of both models in order to better understand and evaluate their overall performance in the characterisation of the PAH. The receptor models were found to be useful in the identification and quantification of PAH source profile and contribution without a prior knowledge of the potential PAH sources impacting in the river sediments. Both models also allowed for the discrimination of four factor/sources, which described PAH profiles and results from their contributions. The quality of both models was shown by regressing the predicted PAH concentration against the measured concentrations. The linear regression estimation gave excellent correlation coefficients PCA-APCS ($r^2 = 0.95$) and PMF ($r^2 = 0.97$). The correlation coefficients and the percentage contributions of PAH underpinned the similarities between the two models and explained the sources of PAH emissions in sediments.

Generally, there was good agreement among the major resolved source emission types between both models, whereby the influence of combustion–related petroleum emissions (diesel and petrol engine emissions) were observed as the most common PAH source. It was also worthy to note that the derived factor solutions shows no apparent order in their arrangement. Hence, the PAH source profile derived from the first factor of the PCA-APCS model was found to be similar to the fourth factor obtained by PMF and vice versa. However, the second and third factors from both models remained largely similar. Furthermore, the second factor derived by PCA-APCS was similar to the corresponding factor obtained by PMF. PCA-APCS was associated with mixed petroleum sources which include: unburned petroleum and

combustion-related petrol emission source as observed by the PAH profile in Figure 4-17. While the source found for PMF may be associated with only petrol emissions as characterized by the dominant HPAH profile shown in Figure 4-24. In addition, the third factors from the PCA – APCS and PMF models provided relatively lesser contributions to the entire source apportionment analysis (2% & 9%, respectively).

Besides the similarities between the factors derived by both models, PCA-APCS differed from PMF in a number of ways. These included the absence of a non-negativity constraint observed in the source contribution profile (Figure 4-16 & Figure 4-18). In this regard, the PAH source contribution obtained by the PCA-APCS model showed negative concentration values in contrast to the source contribution deduced by the PMF model that remained largely positive, thereby presenting a more realistic source apportionment result. Secondly, PMF was able to resolve the problem of negative factor loadings by integrating non-negativity constrained factor analysis, thereby enabling a proper interpretation of factor loadings and scores. In addition, uncertainties associated with the data measurement were considered for PMF with the aid of the method detection limit (MDL) obtained for each PAH compound. In the case of factor 4, traffic-related emissions source was attributed to both models (Figure 4-17 & Figure 4.24). However, PMF was able to resolve more petrol and diesel-related PAH tracers which include PHE and ANT; major tracers of lighter PAH. In general, the PMF model provided a clearer PAH source apportionment approach for the data set provided in this study when compared to the PCA-APCS model.

CHAPTER 5: SUMMARY & CONCLUSIONS

The objective of the study was to determine the levels of polycyclic aromatic hydrocarbons to characterise their sources and apportion their contribution in the sediments from the Brisbane River. The findings from PAH assessment from the study is highlighted below:

The compositional profile revealed that PAH contamination in the river was majorly dominated by pyrogenic sources as evidenced by the predominance of the 4- to 6-ring PAH, particularly fluoranthene (FLT) and pyrene (PYR). From the sediment quality guideline specified in the thesis and comparison with levels of PAHs reported from other locations in Australia and the rest of the world, the marine sediments can be classified as moderately contaminated with less probable ecotoxicological impacts to marine organisms. Furthermore, the sediment physiochemical properties measured such as grain size distribution and total organic carbon were found not to correlate with the total PAH concentrations, showing no significant relationship between them. As a result, hydrodynamic conditions of the river were assumed to have little or no effect on the accumulation of PAHs in the sediments.

A general conclusion was reached from the diagnostic ratio indicators that "combustion sources" are the dominant sources of PAH input in the sediments. Similarly, multivariate analysis employing HCA and PCA identified and classified the PAH compounds into profiles that were characteristic of anthropogenic influences, particularly from petroleum products. Furthermore, results the MCDM

compliment the earlier observations from other multivariate techniques used in the study. PROMETHEE was useful in characterising the PAH pollution levels indicating the least polluted to the highly polluted sites, with the latter mainly found in the industrial section of the river. The ranking pattern from PROMETHEE was comparable to the HCA of the sampling sites, whereas GAIA provided similar information as shown by PCA. As a result, the applicability of the MCDM for site characterisation and ranking in environmental studies was further affirmed. In summary, the combination of multivariate techniques allowed some deeper insights into the identification and classification of the PAH in the river sediments. These findings were reinforced by the use of the receptor models to quantitatively determine the various PAH sources in the Brisbane River.

The application of the PCA-APCS and PMF models provided robust information in the identification of PAH sources. Both models identified four similar factors based on PAH source profile and their relative contributions. The sources revealed the dominance of diesel emissions, particularly from marine vessel and traffic-related emissions (land and marine vehicles) as the largest contributions to PAH input in surface sediment samples, clearly demonstrating influence of anthropogenic activities associated with the sampling sites.

In summary, the study demonstrated the ability of combining multiple multivariate techniques for PAH source apportionment in urban sediments. In other words, future assessment and characterisation of pollutants in sediments from urban water-sheds can benefit from these source identification and apportionment techniques. In addition, the information contained in this thesis can be used as the starting point for

more comprehensive studies on the river and for the planning of the sediment pollution control measures.

5.1. SUGGESTIONS FOR FURTHER WORK

Sediments act as a final sink for aquatic contaminants and also act as a useful matrix for identifying and studying their sources and fate in the environment. As a result, recommendations for proper assessment of contaminants in sediments has outlined below:

With the restriction of the present study to the PAHs only, it is worthy to note that other common organic compounds such as PCBs and pesticides have been reported to be present in sediments from the Brisbane River (Muller et al. 1999; Shaw et al. 2004). Therefore, the source apportionment technique using the PCA-APCS and PMF models may serve as a framework for investigations towards future assessment of this group of compounds. Furthermore, results obtained by the receptor models used for PAH source apportionment can be compared or contrasted against with other apportionment techniques such as the chemical mass balance or UNMIX.

Secondly, the grab sampling technique used for surface sediments sampling in the study was found to be limited in a comprehensive PAH assessment, as it could only account for recent PAH concentrations. Future assessment on the Brisbane River may be carried out by sediment core or profile sampling of bottom sediment and water sampling in addition to the source apportionment techniques in order to account for proper identification of PAH sources in sediments.

Lastly, the result from the thesis has identified a number of anthropogenic activities as potential sources of PAH (i.e. marinas, boat ramps and urban runoff). However the structure of the sediment sampling campaign was not made to specifically address the magnitude of the influence of these activities on sedimentary PAH concentrations. Hence, the sampling campaign can be modified to specifically assess the influences and contribution of a particular source types to the corresponding PAH concentrations obtained.

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APPENDIX 1

Table A1-1: Correlation characteristics of Individual PAHs

	NAP	BNAP	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	B[b+k]F	BaP	IND	DBA	BgP
NAP																
BNAP	0.29															
ACY	0.67**	0.15														
ACE	0.35	-0.08	0.33													
FLU	0.69**	0.12	0.66	0.60*												
PHE	0.43	-0.17	0.42	0.65**	0.50											
ANT	0.22	-0.23	0.27	0.63*	0.45	0.92**										
FLT	0.48	-0.31	0.34	0.15	0.37	0.78**	0.67**									
PYR	0.27	-0.11	0.20	0.08	0.24	0.74**	0.67**	0.88**								
BAA	0.55*	-0.20	0.63*	0.57*	0.51	0.92**	0.77**	0.73**	0.67**							
CHR	0.38	-0.27	0.33	0.51*	0.29	0.90**	0.75**	0.74**	0.77**	0.91**						
B[b+k]F	0.42	0.16	0.55*	0.18	0.46	0.63*	0.46	0.76**	0.73**	0.70**	0.70**					
BAP	0.52*	-0.20	0.59*	0.67**	0.53*	0.82**	0.67**	0.50	0.50	0.91**	0.84**	0.64**				
IND	0.45	-0.32	0.55*	0.57*	0.39	0.84**	0.68**	0.56*	0.57	0.94**	0.88**	0.62*	0.96**			
DBA	0.38	-0.25	0.64**	0.11	0.29	0.62*	0.53*	0.60*	0.59*	0.78**	0.64*	0.67**	0.73**	0.80**		
BGP	0.46	-0.24	0.68**	0.14	0.23	0.64**	0.46	0.63*	0.58*	0.83**	0.69**	0.66**	0.70**	0.83**	0.91**	

**: Correlation is significant at the 0.01 level (2-tailed)

*: Correlation is significant at the 0.05 level (2-tailed)

APPENDIX 2

Table A2-1: Relative TEF potency scheme for indicator priority PAHs.

PAHs	Nisbet and Lagoy, 1992[ab]	Kalberlah et al., 1995[a]	Malcom and Dobson, 1994[a]	USEPA, 1993[ab]	McClure and Schoeny,1995[a]	Muller et al., MOE 1997[a]	Liao et al., 2006[c]
Acenaphthene	0.001	0.001	0.001		-	-	0.001
Acenaphthylene	0.001	0.01	0.001		-	-	0.001
Benz(a)anthracene	0.1	0.1	0.1	0.1	0.1	0.014	0.1
Benzo(a)pyrene	1	1	1	1	1	1	1
Benzo(b)fluoranthene	0.1	0.1	0.1	0.1	0.1	0.11	0.1
Benzo(e)pyrene	-	-	0.01		-	0	0.01
Benzo(ghi)perylene	0.01	0.01	0.01		-	0.012	0.01
Benzo(k)fluoranthene	0.1	0.1	-	0.1	0.1	0.045	0.1
Chrysene	0.1	0.01	-	0.1	0.1	0.026	0.01
Coronene	-	-	-		0.1	0.012	0.001
Dibenz(a,h)anthracene	5	1	1	1	1	0.89	1
Fluoranthene	0.001	0.01	0.001		-	-	0.001
Fluorene	0.001	0	0.001		-	-	0.001
Indeno(1,2,3-cd)pyrene	0.1	0.1	0.1	0.1	0.1	0.067	0.1
Naphthalene	0.001	-	0.001		-	-	0.001
Perylene		-	0.001		-	-	0.001
Phenanthrene	0.001	0	0.001		-	0.00064	0.001
Pyrene	0.001	0.001	0.001		-	0	0.001

Adapted from a:(Knafla et al. 2006); b:(Collins et al. 1998; Liao et al. 2006); c:(Liao et al. 2006)

APPENDIX 3

Table A3-1: Average PAH concentrations (mean ± standard deviation, ng/g) in sediments

PAHs	February 2012	April 2012	June 2012	August 2012	October 2012
NAP	23.5 ± 7.4	22.9 ± 9.0	27.0 ± 7.9	24.9 ± 6.5	21.2 ± 8.3
BNAP	0.8 ± 1.0	1.6 ± 1.3	2.1 ± 1.1	1.7 ± 1.3	2.2 ± 1.1
ACY	3.8 ± 5	4.6 ± 3.5	8.1 ± 6.0	5.6 ± 3.7	5.7 ± 5.1
ACE	0.2 ± 0.6	0.5 ± 1.1	4.9 ± 11.7	1.5 ± 2.1	0.3 ± 1.3
FLU	0.8 ± 1.3	1.4 ± 2.4	3.9 ± 4.2	2.0 ± 2.5	1.1 ± 2.6
PHE	20.2 ± 17	22.3 ± 12.7	27.6 ± 17.6	28.6 ± 20	32.5 ± 14.9
ANT	7.2 ± 8.1	14.0 ± 13.8	15.6 ± 20.2	15.4 ± 19.9	14.7 ± 14.3
FLT	58.9 ± 48.7	78.9 ± 38.8	82.4 ± 42.8	88.0 ± 40.6	113.9 ± 53.4
PYR	65.4 ± 51.5	64.9 ± 45.8	80.8 ± 40.6	95.8 ± 55.8	113.6 ± 71
BAA	34.8 ± 25.7	36.1 ± 18.7	43.2 ± 26.5	45.6 ± 23.2	47.9 ± 27.5
CHR	33.4 ± 26.5	33.1 ± 19.8	29.9 ± 26.3	40.9±22.9	50.7 ± 27.4
B[b+k]F	79.6 ± 70.9	65.3 ± 36	62.9 ± 49.3	69.6 ± 32.4	120.9 ± 63.4
BAP	81.6 ± 95.2	43.1 ± 25.6	48.3 ± 28.9	57.5 ± 30.7	85.5 ± 63.2
IND	79.3 ± 94.7	47.1 ± 23	49.5 ± 26.4	66.9 ± 35.1	75.2 ± 64.6
DBA	8.9 ± 8.2	9.4 ± 3.9	6.6 ± 4.2	10.9 ± 6.9	12.8 ± 12.2
BGP	55.1 ± 47.8	48.4 ± 25.9	36.4 ± 17.7	50.5 ± 33.2	78.6 ± 67.5
ΣPAHs	553 ± 509	536 ± 281	529 ± 331	605 ± 336	776 ± 497